Teaching Portfolio Extracts

This document contains teaching materials that I prepared for two courses that I gave in the Department of Chemistry at the University of Natal at Pietermaritzburg, South Africa. They are felt to be relevant to the application because the processes of analyzing the subject matter and arranging the facts and concepts in a logical way can be expected to be closely similar to the corresponding processes involved in the teaching of mathematics.

The first course presents an introduction to chemical thermodynamics, starting with the basic concepts of work, heat and the conservation of energy, and finishing with the law of chemical equilibrium. This includes a favorable student evaluation of teaching that was conducted by the Centre for University Educational Development.

The second course presents an introduction to statistical thermodynamics, and was delivered to students enrolled for the Honours course in physical chemistry. It embodied a new and original instructional approach whereby the main ideas of a conceptually advanced subject such as this can be presented with a minimum of formal manipulations.

Second Year Physical Chemistry: Thermodynamics

Scope and Significance

The study of chemical thermodynamics at Second Year level is of crucial importance in the education of those who intend to specialise in chemistry or cognate disciplines.

For the intending chemistry major, the most important general goal is the acquisition of skills required for the quantitative description of the the energetics of physical and chemical changes. The first central idea here is the principle of conservation of energy, most generally expressed by the First Law of Thermodynamics, but in a specifically chemical context by Hess's Law and its various equivalent forms. The second idea is that spontaneous processes always proceed in one direction, as summarised by the Second Law of thermodynamics. This leads naturally to the concept of equilibrium as the eventual result of all irreversible processes, and the description of such equilibria in terms of the Gibbs and Helmholtz functions. The most important specific goal of a Second Year course is the derivation of the law of chemical reaction equilibrium from strictly thermodynamic principles, as opposed to the kinetic arguments that are typically used in elementary (First Year) courses.

More generally, the study of thermodynamics can be expected to enhance students' understanding of the nature of energy, and chemical energy in particular. Since usage of energy in some form or other is an inescapable part of everyday reality, many of the practice problems involve application of thermodynamic principles to simple practical situations. As a result of working through these problems, students will enhance their quantitative reasoning and problem-solving skills, as well as their understanding of the underlying concepts.

The mathematical content in treatments of thermodynamics intended for students at this level makes this subject almost universally unpopular. The Laws of Thermodynamics and the properties of the thermodynamic functions are generally expressed by partial differential equations, the significance of which is very unlikely to be appreciated by students who have done only first-year mathematics. The traditional emphasis in such treatments is on the proof of various thermodynamic formulae. As a result, students find it difficult to separate the physical implications of these results from the purely formal manipulations required to obtain them. These deficiencies are compounded by the fact that thermodynamics is usually taught from textbooks on general physical chemistry that attempt to cover everything from chemical kinetics to molecular spectroscopy and quantum theory. The amount of detail that can be devoted to the most conceptually-demanding aspects of thermodynamics is therefore limited.

To counteract the limitations identified above, I have developed a self-contained course in thermodynamics that presents the subject in a way that requires an absolute minimum of formal manipulation with partial derivatives, and focuses instead on simple numerical calculations.

Background of Students

The students taking this course are assumed to have successfully completed Chemistry 110, the physical component of which involves an introduction to the main ideas of atomic structure, stoichiometry, properties of gases, one-component phase equilibrium and colligative properties. Chemical equilibrium is also introduced in the context of reactions involving ideal gas mixtures, acid-base reactions and solubility of ionic solids.

Students are also assumed to have done a first-year mathematics course introducing basic techniques of integral and differential calculus. In connexion with the mathematical background required for thermodynamics it is to be observed that the functions requiring differentiation or integration are considerably simpler than those likely to be encountered in the mathematics courses.

General Aspects of Course Organisation

The course is designed to be given in 14 formal lecture periods. In addition to the notes taken during these lectures (which in general include working of numerical examples) students will receive

- ☐ a brief summary (1-2 pages) of the lecture, in which the main ideas and important formulae are highlighted;
- ☐ a list of specific Learning Objectives, corresponding to the different levels of cognitive skill identified by Bloom (1965);
- ☐ a set of carefully-designed practice problems, individually cross-referenced to the list of Learning Objectives;
- ☐ complete model answers to all these problems. These are considered to be necessary not only to enable students to check their answers, but also to reinforce by example the basic quantitative skills involved. Such skills have an importance that extends far beyond the limits of physical chemistry.

Synopsis of Content and Teaching Strategies

Lecture No. 1

In the first part of this lecture students are reacquainted with the basic physical concepts (such as force, pressure, work, energy and power) that are fundamentally important to the subsequent work in thermodynamics. The generalised dimensions and the relevant SI units are also introduced. Basic manipulations with these physical quantities are illustrated by use of simple examples involving calculation of pressure from force and area, average power from energy consumed in a given time *etc.* The remainder of the lecture is devoted to introducing the concept of a partial derivative, as a natural generalisation of the derivative of a function of one variable, and illustrates the Euler 'chain relation' between partial derivatives of a function of two variables by considering the connexion between the expansion coefficient, compressibility and the derivative of pressure at constant volume.

Lecture No. 2

The purpose of this lecture is to introduce the principle of conservation of energy by consideration of a simple mechanical system obeying Newton's Laws, and to identify the important properties of the mechanical potential energy function, *viz.*, that only differences in potential energy are physically significant, that these differences depend only on the initial and final points, and that positions of equilibrium correspond to maxima and minima in potential energy. The relation between quantities of heat transferred between bodies at different temperatures is then introduced by consideration of several simple examples. Finally the First Law is presented as a generalization of the principle of energy conservation that applies to generation of heat as well as performance of mechanical work.

Lecture No. 3

This lecture starts by identifying the most important properties of the Internal Energy function, particularly in comparison with the mechanical potential energy. The work involved in changing the volume of a system is then introduced with specific reference to a perfect gas, and the distinction between reversible and irreversible expansions noted. Consideration of special cases of the First Law where either the volume or pressure is constant is then used to introduce the Enthalpy function, and the corresponding heat capacities at constant pressure and at constant volume. The expression for the difference in the heat capacities is derived, and interpreted in terms of the work done by a substance in expanding against its cohesive forces.

Lecture No. 4

This lecture is devoted to consideration of reversible and irreversible adiabatic expansions of perfect gases, and introduces the heat capacity ratio γ. Consideration of adiabatic processes is justified by mentioning their importance in the theoretical analysis of internal combustion engines and propagation of sound waves, but no further details of these applications are given. The main aim here is to develop the idea of the internal energy change as the work involved in an adiabatic process, thereby making possible a purely mechanical definition of heat.

Lecture No. 5

The goal of this lecture is to introduce the Joule-Thomson Effect as a direct consequence of the existence of cohesive forces between gas molecules. The lecture begins with a description of this general idea, followed by derivation of the relation between the constant-pressure heat capacity and the isenthalpic and isothermal Joule-Thomson coefficients. The practical importance of the Joule-Thomson Effect in the operation of refrigerators is described, and the lecture concludes with numerical examples illustrating the typical values of the temperature change achievable by a given pressure drop.

Lecture No. 6

In this lecture, a molecular interpretation for the heat capacities of ideal gases is developed. The various ways in which molecules can absorb energy are identified, and the concept of 'mechanical degrees of freedom' is introduced. The determination of the number of mechanical degrees of freedom is then illustrated for both linear and nonlinear molecules. A qualitative description of the harmonic oscillator model for a vibrating bond is given, and the Equipartition Principle is stated. The lecture concludes with a comparison between experimental molar heat capacities and those predicted by the Equipartition Principle, and a qualitative explanation for the discrepancy in terms of the quantum theory.

Lecture No. 7

The subject of thermochemistry is introduced by considering the experimental aspects of calorimetry, in particular, the relation between the enthalpy and internal energy changes and how calorimeters can be calibrated by electrical generation of a precisely-known quantity of heat. It is worth considering this latter point in detail, because all domestic electrical heaters operate on the same principle (Joulean heat evolution). Hess's Law of Constant Heat Summation is then introduced as the application of the First Law to chemical reactions, and the lecture is concluded by summarising the rules that apply in the determination of enthalpy changes by addition and subraction of reactions.

Lecture No. 8

Thermochemical calculations are illustrated in detail in this lecture by determining the heats of formation for cyclohexane, cyclohexene, cyclohexadiene and benzene from combustion enthalpy data. The enthalpies of formation so determined are then used to calculate the enthalpies of hydrogenation for cyclohexene, cyclohexadiene and benzene to cyclohexane, and Hess's Law is illustrated by obtaining the same results directly from the combustion enthalpies. Comparison of the enthalpies of hydrogenation for the three unsaturated compounds leads naturally to an average enthalpy per double bond, and the concept of resonance stabilization. The lecture concludes with a discussion of how enthalpies of formation can be determined by addition of individual bond enthalpies, and the assumptions and errors inherent in such estimates.

Lecture No. 9

The procedures illustrated in the previous lecture are summarised by statement of the general expression for the enthalpy of an arbitrary reaction in terms of the enthalpies of formation of all products and reactants, and the implied convention regarding the enthalpies of formation of elements in their standard states is discussed. The use of thermodynamic cycles for the estimation of enthalpy changes is introduced by consideration of the problem of calculating the enthalpy of vaporization of a liquid at a temperature lower than its boiling point, and this is subsequently generalised to an approximate expression for the temperature-dependence of the enthalpy of an arbitrary reaction in terms of the heat capacities of participating species. Finally the Born-Haber cycle is introduced by considering the estimation of lattice energies of ionic solids.

Lecture No. 10

The concept of a cyclic mechanical process is introduced as a continuation of the previous work on thermochemical cycles, and used to introduce the entropy as the quantity of heat transferred divided by the temperature of the transfer. The Carnot cycle is chosen as a particular example, not because it is a convincing model for an actual device, but because application of the First Law to each step of it shows that the entropy change around the cycle is zero. Neither the Carnot cycle nor any other mechanical cycle is considered further; it is felt that the more detailed discussions that are presented in most textbooks are a digression that is more likely to confuse than enlighten students. The general result that the entropy change is zero around any reversible cycle is merely stated without proof. The lecture is concluded by consideration of the calculation of entropy changes for simple processes, such as the reversible isothermal expansion of perfect gases and the reversible vaporization of a liquid at its boiling point. The concept that a positive entropy change is generally associated with formation of more disordered molecular arrangements is also introduced.

Lecture No. 11

The calculation of the entropy change associated with raising or lowering the temperature of a substance is introduced as a generalisation of the definition of entropy presented in the previous lecture. Attention is then turned to the estimation of the entropy change experienced by the environment as a result of loss or gain of heat by the system. This leads naturally to the statement of the Second Law, that the direction of spontaneous processes is that in which the combined entropy of the system and the environment increases. The remainder of the lecture is devoted to demonstrating the equivalence of this statement and other versions of the Second Law.

Lecture No. 12

In this lecture, processes that are known to be irreversible are analysed to determine the entropy changes experienced by the system and the environment. The emphasis on calculations of entropy changes in specific irreversible processes is a significant point of departure from conventional treatments, which are content to state the Second Law in the form of a differential and move on. It is felt that it is only through calculations of this kind that a good feeling for how the Second Law operates can be gained. The processes considered include irreversible cooling, volume changes and phase transitions, and have been selected to enable the students to be able to identify whether the system or the environment experiences the greater entropy change.

Lecture No. 13

The molecular interpretation of entropy is introduced by observing that the irreversible processes considered earlier have in common a tendency to equilibrium. In statistical-mechanical terms, the equilibrium arrangement corresponds to the most probable molecular arrangement available to a system of given size and total energy. The Boltzmann formula for the entropy is stated, without proof. The macroscopic and microscopic views of entropy are brought together by consideration of the Third Law: the zero entropy associated with a perfect crystal is made quite plausible by invoking Boltzmann's formula. The lecture concludes with the alternative statements of the Second Law in terms of the Gibbs and Helmholtz functions, and the significance of these functions in relation to the maximum work that can be performed by the system.

Lecture No. 14

This lecture contains most of the formal manipulations required in the course. The most important goal is the determination of the pressure and temperature dependence of G, from which follows the definition of the fugacity. The starting point is the differential equation expressing the combined First and Second Laws, which itself is derived by applying a limiting procedure to the finite change in internal energy corresponding to finite temperature and volume changes. To obtain the required result it is necessary to apply successive Legendre transformations to the Combined First and Second Laws, which requires expressions for the differentials of the products pV and TS: these differentials are themselves derived by a limiting procedure. Straightforward algebra then leads to the result $dG = Vdp - SdT$. The dependence of G on p for an ideal gas is introduced and generalised to give the relation between the chemical potential and the fugacity. Finally, the law of chemical equilibrium is stated for a reaction between gases.

Bibliography

In developing this course I have compared the developments of thermodynamic concepts presented in many published textbooks, and have attempted to combine the best elements of each. Those texts that I have found most useful are as follows.

Atkins, P.W. (1990). "Physical Chemistry", 4th ed., Oxford University Press. This is probably the most widely-used textbook on general physical chemistry. It is probably not suitable for students with rather weak mathematical backgrounds.

Barrow, G.M. (1973). "Physical Chemistry", 3rd ed., McGraw-Hill. This text develops macroscopic and microscopic views of matter in parallel, which I think might tend to confuse students: thermodynamic results are necessarily independent of molecular models. The use of the Second Law to suggest the definition of the Gibbs function is good.

Moore, W.J. (1972). "Physical Chemistry", 5th ed., Longmans. The analogy between the mechanical potential energy and the internal energy function is developed very thoroughly.

Dasent, W.J. (1970). "Inorganic Energetics", Penguin Books. Presents very detailed discussion of the application of Born-Haber cycles to estimation of lattice energies etc.

Bromberg, J.P. (1980). "Physical Chemistry", Allyn and Bacon. Problems contain quite a few applications to biological systems.

Physical Chemistry Lecture 1: Summary

Thermodynamics is the study of energy relationships associated with physical and chemical transformations of substances. We begin our study of this subject by revising some physical concepts that are fundamentally important to the more specific results to be covered later.

The first of these concepts is that of a *force*. The effect of a force is to change the velocity of an object, or to prevent an object from moving. Dimensions of force are M L T^{-2}, where M, L and T are the fundamental units of mass, length and time. In the SI system, these fundamental units are the kilogram, the metre and the second, respectively, and the composite unit kg m s^{-2} is referred to as the newton (N).

A force is distributed over an area is often described by the ***pressure***, which is equal to the force divided by the area. The generalised dimensions of pressure are M L^{-1} T^{-2}. In the SI system, pressure is expressed in pascal (Pa) or newton per square metre, which is equivalent to kg m^{-1} s^{-2}.

When an application of a force causes an object to move, ***work*** is said to be performed. The work done is equal to the product of the force and the distance moved. The capacity to do work is referred to as *energy*, and as we shall see, the performance of any sort of work requires the consumption of some kind of energy. General dimensions of work and energy are M L^2 T^{-2}. In the SI system, work is measured in joule or newton metre, equivalent to kg m^2 s^{-2}.

The rate at which work is done or energy is consumed is known as the *power*, which is accordingly expressed in the dimensions M L^2 T^{-3}. The SI unit of power is the watt (W), which corresponds to the expenditure of one joule per second. In terms of the fundamental units, W = kg m^2 s^{-3}.

Many important measurements in thermodynamics yield values of the rate of change or derivative of one quantity with respect to another. Furthermore, since thermodynamic quantities are in general functions of more than one independent variable, these rates of change can be expected to depend on which independent variables are held constant. As a result, thermodynamic formulae very often involve partial derivatives. An example of a partial derivative is the quantity

$$\left(\frac{\partial p}{\partial T}\right)_V,$$

which is read as, 'the partial derivative of p with respect to T at constant V'. Knowledge of the value of derivatives allows estimates to be made of the change of one variable corresponding to a change in the other. For example, for mercury at 323 K, the above partial derivative is 46.2 atm K^{-1}. Therefore, when the temperature of a sample of mercury confined to constant volume increases from 323 K to 325 K, the corresponding increment of pressure is

$$\delta p \simeq \left(\frac{\partial p}{\partial T}\right)_V \delta T = (46.2\ \text{atm K}^{-1}) \times (2\ \text{K}) = 92.4\ \text{atm}.$$

This is typical of the calculations for which thermodynamic partial derivatives are used. This type of relation between corresponding increments is in general to be regarded as approximate, since the derivatives themselves can be expected to depend on the variables concerned. However, this dependence can sometimes be neglected to an excellent approximation. Increments of functions of several variables can clearly be made for each independent variable. For example, if the volume of a substance is regarded as a function of temperature and pressure, the increment of volume corresponding to simultaneous increments in p and T is given by

$$\delta V = \left(\frac{\partial V}{\partial T}\right)_p \delta T + \left(\frac{\partial V}{\partial p}\right)_T \delta p + \ldots.$$

The additional terms not shown in this equation involve higher partial derivatives and higher powers of δT and δp, and are negligible if these increments are sufficiently small. In this limit, the expression reduces to the *total differential* of V with respect to T and p:

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp$$

If the quantities dT and dp are chosen in such a way that dV is zero, a relation can be established between the two partial derivatives of V and the partial derivative of p with respect to T. This can be derived by dividing dp by dT and transposing terms:

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}.$$

The three partial derivatives in this equation are of importance because, as we will see in subsequent lectures, their values reflect the strength of cohesive forces in the substance. Since the volume is an extensive quantity (*i.e.*, depends on the quantity of substance), the dependence of volume on pressure and temperature is usually expressed in terms of the thermal expansivity,

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

and the isothermal compressibility,

$$\beta \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T.$$

The negative sign is included here because volume must decrease with increasing pressure. These quantities give the *relative* or *fractional* change in volume with temperature or pressure.

Learning Objectives:

Knowledge

1.1.1 Express physical quantities such as force, pressure, work, energy and power in terms of general dimensions mass M, length L and time T and in terms of SI units.

1.1.2 State the following physical relationships:

(i) force in terms of mass and acceleration
(ii) work in terms of force and distance
(iii) pressure in terms of force and area
(iv) relation between power and energy consumption over time

1.1.3 Define isothermal compressibility and isobaric thermal expansivity.

Comprehension

1.2.1 Write expressions for the increment of functions of one or several variables.

1.2.2 Explain why a negative sign is used in the definition of the isothermal compressibility but not in the thermal expansivity.

Application

1.3.1 Perform simple calculations of force, pressure, work/energy, and power.

1.3.2 Use values of partial derivatives to relate increments of dependent and independent variables.

1.3.3 Determine fractional volume changes from pressure and temperature increments and *vice versa*, given values of compressibility and thermal expansivity.

Analysis

1.4.1 Set up relations between partial derivatives of a function of two variables in the manner illustrated for the volumetric derivatives.

Problems

Acceleration due to gravity is 9.807 m s^{-2}.

1.1 Find the force exerted on a horizontal surface by a mass of 1 kg.
[1.1.2(i),1.3.1]

1.2 Determine the pressure if the weight of the mass in problem 1 is distributed over (a) 100 cm^2, and (b) over a pin-point of area 0.01 mm^2.
[1.1.2(iii),1.3.1]

1.3 What work must be done against the force of gravity in lifting an object of mass 3 kg 50 m above the surface of the earth?
[1.1.2(ii),1.3.1]

1.4 Calculate the average power involved in lifting the mass of question 4 in 30 s.
[1.1.2(iv),1.3.1]

1.5 Domestic energy consumption is usually measured in kilowatt hours (kWh). What is the equivalent in joules?
[1.1.2(iv),1.3.1]

1.6 An electric jug with a rated power of 1.5 kW boils a cup of water in 60 s. Calculate the amount of energy consumed in (a) joule (b) kWh.
[1.1.2(iv),1.3.1]

1.7 The 'calorie', formerly used in dietetics as a measure of energy yield, is equal to 4.184 kJ. Calculate the average power of a human being consuming 2000 'calories' per day.
[1.1.2(iv),1.3.1]

1.8 The isothermal compressibility of Pb at 300 K is 2.21×10^{-6} atm^{-1}. What is the fractional decrease in volume of a sample of Pb resulting from an increase in p of 100 atm?
[1.3.3]

1.9 The isobaric thermal expansivity of benzene at 1 atm and 293 K is 1.24×10^{-3} K^{-1}. Assuming this to be constant, estimate the temperature increase required to cause a fractional increase in volume of 0.5%.
[1.3.3]

1.10 A thermodynamic quantity U depends on temperature T and volume V. By following the same argument as demonstrated for the volumetric partial derivatives, establish a relation between the quantities

$$\left(\frac{\partial U}{\partial T}\right)_V, \quad \left(\frac{\partial U}{\partial V}\right)_T, \quad \text{and} \quad \left(\frac{\partial T}{\partial V}\right)_U .$$

[1.2.1,1.4.1]

Solutions: Lecture 1.

1.1 The force is equal to the product of the mass and the acceleration due to gravity. Thus,

$$F = (1\text{ kg}) \times (9.807\text{ m s}^{-2}) = 9.807\text{ N.}$$

1.2 The areas involved here are respectively 10^{-2} m^2 and 10^{-8} m^2. The corresponding pressures are therefore

$$\text{(a) } p = \frac{(9.807\text{ N})}{(10^{-2}\text{ m}^2)} = 980.7\text{ Pa} \qquad \text{(b) } p = \frac{(9.807\text{ N})}{(10^{-8}\text{ m}^2)} = 9.807 \times 10^{8}\text{ Pa.}$$

1.3 Work is the product of force and distance:

$$w = Fd = (3\text{ kg}) \times (9.807\text{ m s}^{-2}) \times (50\text{ m}) = 1.471\text{ kJ.}$$

1.4 Average power is the work divided by the time taken:

$$P = \frac{w}{t} = \frac{(1\,471\text{ J})}{(30\text{ s})} = 49.04\text{ W.}$$

1.5 1 J is equal to 1 W s. Therefore

$$1\text{ kWh} = (1\,000\text{ W}) \times (3\,600\text{ s}) = 3.6\text{ MJ.}$$

1.6 Amount of energy is equal to power times time. Therefore,

$$\text{Energy} = (1.5\text{ kW}) \times (60\text{ s}) = 90\text{ kJ} = 0.025\text{ kWh.}$$

1.7 The total energy consumed by the person in one day is

$$2000\text{ 'calories'} = 2000 \times 4.184\text{ kJ} = 8.368\text{ MJ.}$$

The average power is obtained by dividing this quantity by the length of one day in seconds:

$$\text{power} = \frac{(8.368 \times 10^{6}\text{ J})}{(24\text{ h}) \times (3.6 \times 10^{3}\text{ s h}^{-1})} = 97\text{ W.}$$

This is a little less than the rate of energy consumption of a typical light bulb.

1.8 Applying the definition,

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \quad \Rightarrow \quad -\frac{\delta V}{V} \simeq \beta p = (2.21 \times 10^{-6}\ \text{atm}) \times (100\ \text{atm})$$

$$= 2.21 \times 10^{-4},$$

or about 0.02%.

1.9 Applying the definition,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_T \quad \Rightarrow \quad \frac{\delta V}{V} \simeq \alpha \delta T$$

$$\delta T \simeq \frac{1}{\alpha}\frac{\delta V}{V} = \frac{(0.005)}{(1.24 \times 10^{-3}\ \text{K}^{-1})} = 4.03\ \text{K}.$$

1.10 The total differential of U as a function of T and V is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV.$$

Setting $dU = 0$ (*i.e.* requiring that U is constant),

$$\left(\frac{\partial U}{\partial T}\right)_V dT = -\left(\frac{\partial U}{\partial V}\right)_T dV,$$

and dividing dT by dV and transposing terms results in

$$\left(\frac{\partial T}{\partial V}\right)_U = -\frac{\left(\frac{\partial U}{\partial V}\right)_T}{\left(\frac{\partial U}{\partial T}\right)_V}.$$

Physical Chemistry Lecture 2: Summary

In classical mechanics, the position and velocity of objects can be determined completely from their initial positions and velocities and knowledge of the forces acting upon them. The crucial relation which makes this possible is Newton's Second Law of Motion:

$$\mathbf{F}_i = m_i \frac{\mathrm{d}\mathbf{v}_i}{\mathrm{d}t} \tag{1}$$

where $\mathbf{F}_i$ and $\mathbf{v}_i$ are the force and velocity vectors for each particle i of mass m_i in the system, and t is the time. Application of Newton's Law to each object results in a collection of differential equations, which can be solved analytically only for simple systems containing one or two particles.

The most important characteristic of classical mechanics is the idea of *interconversion of kinetic and potential energy*. To demonstrate how this works, consider the simple case of a single particle acted on by a force that depends only on the distance r from some origin. From the equation of motion, it is possible to relate the amount of work required to move the particle between points r_0 and r_1 to the difference in kinetic energy between these two points:

$$F(r) = m\frac{\mathrm{d}v}{\mathrm{d}t} = m\frac{\mathrm{d}^2 r}{\mathrm{d}t^2} \tag{2}$$

$$w = \int_{r_0}^{r_1} F(r)\,dr = m\int_{r_0}^{r_1} \frac{d}{dt}\left(\frac{dr}{dt}\right) dt$$

$$= \frac{1}{2}mv_1^2 - \frac{1}{2}mv_0^2. \tag{3}$$

The force can also be related to the potential energy $u(r)$ by the equation

$$F = -\frac{du}{dr} \tag{4}$$

Potential energy is defined as the work required to bring the particle from infinity (where the force is zero) to some distance r, so the work expressed by equation 3 is also equal to

$$w = -\int_{r_0}^{r_1} \frac{du}{dr}\,dr = u(r_0) - u(r_1). \tag{5}$$

Equating the right-hand sides of equations (3) and (5) and combining terms, we obtain

$$u(r_0) + \frac{1}{2}mv_0^2 = u(r_1) + \frac{1}{2}mv_1^2. \tag{6}$$

Thus, the sum of kinetic and potential energy does not change. Three more important ideas emerge from consideration of the above simple model. First, the work expressed by equation (3) is seen to depend only on the points r_0 and r_1 and not on the path taken between these points. Second, it is also clear from equations (4) and (5) that only the *difference* in potential energy proves to be physically significant. Third, if the potential energy assumes a maximum or minimum value, the force becomes zero and a *point of equilibrium* is said to be reached. This equilibrium is said to be stable or unstable depending on whether the potential energy is a minimum or maximum, respectively.

While the above equations show that potential and kinetic energy can be interchangeable, there is no way that the analysis can account for the conversion of kinetic energy into heat by velocity-dependent frictional forces.

The subject of thermodynamics came into being from the observations that heat could be generated from performance of mechanical work (as in cutting or drilling of materials), and that mechanical work could be produced from heat input (as in the steam engine). Careful experiments by Joule, Helmholtz and others led to the formulation of a more general principle of conservation of energy that applied to both heat and mechanical work. This is now known as the **First Law of Thermodynamics**, and can be stated as follows:

> "In a transition between two equilibrium states of a system, the sum of the amount of work done on a system and the heat supplied to it is a constant, depending only on the initial and final states."

or,

$$\Delta U = q + w.$$

The value of the constant is the change in the *internal energy function*, U, for the system. The amount of work corresponding to a given amount of heat is expressed by the *mechanical equivalent of heat*, which is 4.184 joule per calorie, where one calorie is the amount of heat required to raise the temperature of 1 g water from 15°C to 16°C.

The quantities of heat implied in the statement of the First Law are determined by measurement of changes in temperature of objects of precisely known properties. The simplest relation between the quantity of heat, quantity of substance and the temperature change is

$$q = nc\,\Delta T \qquad (8)$$

where n is the number of moles, and the specific heat c is the amount of heat required to raise one mole of substance by 1 K. Specific heat can also be defined per unit mass rather than per mole, but this is not commonly used in chemical thermodynamics. In general, the specific heat depends on temperature, and the equation

$$q = m\int_{T_1}^{T_2} c(T)\,dT \qquad (9)$$

must be used in place of equation 8. Over small temperature ranges, the variation of heat capacity can be neglected for many substances.

Learning Objectives

Knowledge

2.1.1 State the following physical relationships:

(i) relation between the temperature change and quantity of heat
(ii) The First Law of Thermodynamics

Comprehension

2.2.1 Distinguish between statements of the First Law in which work is done *on* or *by* the system.

Application

2.3.1 Calculate the quantity of heat required to raise the temperature of an object with constant heat capacity.

2.3.2 Calculate the quantity of heat required to raise the temperature of an object with temperature-dependent heat capacity.

Problems

2.1 The heat capacity of Al is 24.35 J K^{-1} mol^{-1}. Calculate the heat input required to raise the temperature of a 100 g block of Al by 3.8 K, assuming that the heat capacity is constant (molar mass of Al = 26.98 g mol^{-1}).

[2.3.1]

2.2 State the relation between the heat suplied to a system, the work done by it, and the change in the internal energy.

[2.1.1(i),2.2.1]

2.3 The heat capacity of air at room temperature and atmospheric pressure is about 21 J K^{-1} mol^{-1}. How much heat is required to raise the temperature of a room of dimensions 5m x 6m x 4m by 10°C? Neglecting losses, determine how long a 1.5 kW heater would have to operate to achieve this temperature increase.

[2.1.1(i),2.3.1]

2.4 Many important experiments devised by Joule involved the conversion of mechanical energy into heat, for example, by arranging a falling weight to stir water by turning a paddle wheel. In one such experiment, a mass of 6.00 kg fell through a height of 50.0 m and stirred 0.600 kg of water initially at 15°C. Assuming that all the potential energy was converted into heat, calculate the final temperature of the water. At 15°C, the heat capacity of water is 4.184 J g^{-1}; assume that this is constant over the temperature range encountered.

[2.3.1]

2.5 The molar heat capacity of Ag in the temperature range 50 K < T < 100 K is given by the empirical equation

$$c_p = -0.63 + 0.32T - 1.1 \times 10^{-3}T^2$$

Calculate the quantity of heat required to raise the temperature of 300 g Ag from 55 K to 98 K (molar mass of Ag = 108 g mol^{-1}).

[2.3.2]

Solutions

2.1 It is first necessary to determine the number of moles:

$$n = \frac{(100\ \text{g})}{(26.98\ \text{g mol}^{-1})} = 3.706\ \text{mol}$$

The heat required is therefore

$$\begin{aligned} q &= nc_p\,(T_2 - T_1) \\ &= (3.706\ \text{mol}) \times (24.35\ \text{J K}^{-1}\text{mol}^{-1}) \times (3.8\ \text{K}) \\ &= 342.9\ \text{J} \end{aligned}$$

2.2 If w is the work done by a system and q is the heat supplied to it, then the internal energy change is

$$\Delta U = q - w$$

2.3 The number of moles of air contained in the room of volume 4 m x 5 m x 6 m = 120 m^3 is

$$\begin{aligned} n &= \frac{pV}{RT} \\ &= \frac{(1.013 \times 10^5\ \text{Pa}) \times (120\ \text{m}^3)}{(8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (298\ \text{K})} \\ &= 4906\ \text{mol.} \end{aligned}$$

The quantitiy of heat is therefore

$$\begin{aligned} q &= nc_p(T_2 - T_1) \\ &= (4.906 \times 10^3\ \text{mol}) \times (21\ \text{J K}^{-1}\text{mol}^{-1}) \times (10\ \text{K}) \\ &= 1.030\ \text{MJ.} \end{aligned}$$

At a rate of 1.5 kW = 1.5 kJ s^{-1}, this would be delivered in a time

$$t = \frac{(1.030 \times 10^6\ \text{J})}{(1.5 \times 10^3\ \text{J s}^{-1})} = 687\ \text{s}$$

or just over 11 minutes.

2.4 Represent the mass of the weight by M and the specific heat per unit mass of water by c. The change in mechanical potential energy of the weight is

$$\begin{aligned} \Delta u &= Mgh \\ &= (6.00\ \text{kg}) \times (9.81\ \text{m s}^{-2}) \times (50.0\ \text{m}) \\ &= 2.94\ \text{kJ.} \end{aligned}$$

On complete conversion to heat, this will result in a temperature T which satisfies the equation

$$q = \Delta u = mc(T - 288)$$

$$T = \frac{\Delta u}{mc} + 288$$

$$= \frac{(2.94\ \text{kJ})}{(0.600\ \text{kg}) \times (4.184\ \text{kJ kg}^{-1})} + 288$$

$$= 289.2\ \text{K}.$$

2.5 The number of mol of silver is

$$n = \frac{(300\ \text{g})}{(108\ \text{g mol}^{-1})} = 2.778\ \text{mol}.$$

The heat required is therefore

$$q = n \int_{T_1}^{T_2} c_p\, dT$$

$$= n \int_{T_1}^{T_2} [- 0.63 + 0.32T - 0.0011T^2]\, dT$$

$$= n\,[- 0.63 + 0.32\frac{T_2^2 - T_1^2}{2} - 0.0011\frac{T_2^3 - T_1^3}{3}]$$

With $T_1 = 55$ K, $T_2 = 99$ K and $n = 2.778$ mol

$$q = (2.778\ \text{mol}) \times [- 0.63(98 - 55) + 0.32(98^2 - 55^2) - 0.0011\frac{98^3 - 55^3}{3}]$$

$$= 2.2\ \text{kJ}$$

Physical Chemistry Lecture 3: Summary

The internal energy function introduced in the previous lecture is similar to the mechanical potential energy in that the change in the internal energy depends only on the initial and final states of the system. This is to be contrasted with the heat and work terms, which both depend on the way in which processes are carried out. Another point of similarity is that only differences in internal energy are physically significant. Absolute values of internal energy can be defined only by adoption of an arbitrary convention. The difference between internal energy function and mechanical potential energy is that mechanical potential energy is a measure of the capacity to do work, whilst U is a measure of the capacity to do work and supply heat.

In applying the First Law to the analysis of mechanical processes involving gases, it is convenient to introduce the concept of a reversible process. This is one in which the system passes through a continuous sequence of equilibrium states in going from the initial state to the final state. In a reversible compression or expansion, the pressure is related to the volume by an equation of state, for each intermediate volume. In practice, complete reversibility cannot be achieved, because of the finite time required for gases to reach equilibrium. The general formula for the work involved in a reversible volume change for a gas is

$$w = -\int_{V_1}^{V_2} p\, dV \qquad (1)$$

and for an ideal gas at constant temperature, this yields the result

$$w = -nRT \ln \left(\frac{V_2}{V_1}\right). \qquad (2)$$

Since for an ideal gas the internal energy depends only on the temperature, the internal energy change for such an isothermal compression or expansion is zero, so that application of the First Law gives the result

$$\Delta U = q + w = 0 \quad \text{or} \quad q = -w. \qquad (3)$$

The other important case is where a gas or other substance expands against or is compressed by a constant pressure. Here, the work involved is

$$w = -p\,(V_2 - V_1). \qquad (4)$$

From these results it is clear that when the change in volume is zero, no work is possible. Therefore the internal energy change can be identified as the heat absorbed at constant volume:

$$\Delta U = q_V. \qquad (5)$$

The heat absorbed at constant volume can be in turn related to the corresponding temperature change by definition of the constant volume heat capacity c_V:

$$c_V = \left(\frac{\partial U}{\partial T}\right)_V. \qquad (6)$$

If heat is absorbed constant pressure, the system can do work by expanding against this pressure, and application of the First Law leads to the result

$$\Delta U = q_p - p\Delta V \quad \text{or} \quad q_p = \Delta H = \Delta U + p\Delta V \qquad (7)$$

where the function H is referred to as the enthalpy or heat content. The heat capacity at constant pressure is defined by

$$c_p = \left(\frac{\partial H}{\partial T}\right)_p. \qquad (8)$$

At constant volume a substance can respond to the absorption of heat only by raising its temperature, while at constant pressure, it can respond by changing its volume (*i.e.*, performing work) as well as raising its temperature. We therefore expect that c_p will be greater than c_V. The starting point in the calculation of the heat capacity difference is the expression for the differential of U as a function of T and V, viz.

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV. \tag{9}$$

Dividing by dT and imposing the condition of constant pressure, we obtain

$$\left(\frac{\partial U}{\partial T}\right)_p = c_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p, \tag{10}$$

which is in turn substituted into the definition of the constant pressure heat capacity :

$$\left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_V = c_V + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{11}$$

or, in terms of the thermal expansivity,

$$c_p - c_V = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\alpha V. \tag{12}$$

The isothermal derivative of U with respect to V is called the *internal pressure*, and is a direct measure of the strength of cohesive forces in the substance. For the special case of an ideal gas, the internal pressure is identically zero and equation 12 reduces to

$$c_p - c_V = R. \tag{13}$$

Learning Objectives

Knowledge

3.1.1 State the following physical relationships:

(i) work of expansion/compression for reversible process
(ii) work of expansion/compression for irreversible process

Comprehension

3.2.1 Distinguish between heat absorbed at constant volume and constant pressure and use this distinction to define internal energy and enthalpy functions.

3.2.2 Explain qualitatively why the internal pressure of a substance is in general different from zero.

3.2.3 Describe the dependence of U on V for a perfect gas.

3.2.4 Explain the physical origin of the difference between c_p and c_V.

Application

Calculate:

3.3.1 work and heat transfers involved in reversible isothermal expansion/compression of an ideal gas.

3.3.2 work and heat transfers involved in irreversible isothermal expansion/compression of an ideal gas.

3.3.3 internal energy and enthalpy changes resulting from heat input and performance of work.

3.3.4 internal pressure from heat capacity difference.

Analysis

Justify steps involved in the derivation of the relations:

3.4.1

$$C_p - C_v = [p + (\frac{\partial U}{\partial V})_T](\frac{\partial V}{\partial T})_p \equiv p\,(\frac{\partial V}{\partial T})_p + (\frac{\partial U}{\partial V})_T(\frac{\partial V}{\partial T})_p$$

3.4.2

$$(\frac{\partial U}{\partial T})_p = C_v + \alpha V\,(\frac{\partial U}{\partial V})_T$$

Problems

3.1 The constant-volume heat capacity of Ar is 12.47 J K^{-1} mol^{-1}. Calculate the change in internal energy when a sample of Ar at 298 K and 1 atm pressure, confined to a volume of 15.36 L, absorbs 36.23 J of heat. What is the final temperature of the gas?

[3.2.1,3.3.3]

3.2 Consider the equation

$$(\frac{\partial U}{\partial T})_p = (\frac{\partial U}{\partial T})_V + (\frac{\partial U}{\partial V})_T(\frac{\partial V}{\partial T})_p \qquad (1)$$

(i) Derive this equation, starting from the expression for the total differential of U as a function of T and V.

[3.4.2]

(ii) What are the dimensions (in general units mass M, length L, time T etc.) of the quantity

$$(\frac{\partial U}{\partial V})_T\,?$$

Explain why this quantity should be in general different from zero.

[3.2.2,1.1.1]

(iii) By considering the change in internal energy of a substance with temperature and at constant pressure, give a physical interpretation of equation (1).

[3.2.4]

3.3 Justify each step in the following derivation:

$$\begin{aligned} c_p - c_V &= (\frac{\partial H}{\partial T})_p - (\frac{\partial U}{\partial T})_V \\ &= (\frac{\partial U}{\partial T})_p + p\,(\frac{\partial V}{\partial T})_p - (\frac{\partial U}{\partial T})_V \\ &= [p + (\frac{\partial U}{\partial V})_T](\frac{\partial V}{\partial T})_p \\ &= [p + (\frac{\partial U}{\partial V})_T]\alpha V \end{aligned}$$

[3.4.1,3.4.2]

3.4 For 1 mol of benzene at 1 atm, $\alpha = 1.24 \times 10^{-3}$ K^{-1}, $V = 88.77$ cm^3 and the difference between the heat capacities is $c_P - c_V = 45$ J K^{-1} mol^{-1}. Calculate the internal pressure, and comment on the size of your result.

[3.2.4,3.3.4]

Solutions

3.1 We are given the pressure and temperature of the constant-volume gas sample. It is first necessary to work out the number of moles:

$$n = \frac{pV}{RT} = \frac{(1.013 \times 10^5 \text{ Pa}) \times (1.536 \times 10^{-2} \text{ m}^3)}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})} = 0.6280 \text{ mol}$$

The change in internal energy is equal to the heat absorbed at constant volume, *i.e.* $\Delta U = 36.23$ J. The final temperature T satisfies

$$q = nc_V(T - 298)$$

i.e.,

$$T = 298 + \frac{(36.23 \text{ J})}{(0.6280 \text{ mol}) \times (12.47 \text{ J K}^{-1}\text{mol}^{-1})}$$

$$= 298 + 4.6$$

$$= 302.6 \text{ K}$$

3.2(i) Considering U as a function of T and V, the total differential is

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

At constant pressure, the differential of V is

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT$$

so that

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p dT$$

Dividing both sides by dT gives

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

which is the required result.

(ii) The dimensions of internal energy and volume are, respectively,

$$[U] = \text{M}\,\text{L}^2\,\text{T}^{-2}$$

$$[V] = \text{L}^3$$

The derivative of internal energy with respect to volume therefore has dimensions

$$\left[\left(\frac{\partial U}{\partial V}\right)_T\right] = \frac{\text{M}\,\text{L}^2\,\text{T}^{-2}}{\text{L}^3} = \text{M}\,\text{L}^{-1}\,\text{T}^{-2}.$$

which is clearly the same as force per unit area or pressure:

$$\frac{\mathrm{M\,L\,T^{-2}}}{\mathrm{L^2}}$$

This derivative is referred to as the *internal pressure*, and its value reflects the strength of cohesive forces in the substance.

(iii) The first term on the right hand side of the equation gives the change in internal energy resulting from the temperature change alone, and the second term expresses the change in internal energy resulting from a change in volume alone. In this situation, the volume change itself results from the change in temperature, as expressed by the derivative of volume with respect to temperature.

3.3 Line 2: This follows from the definition of enthalpy, $H = U + pV$.

Line 3: This follows from the identity proved in part (c) of the preceding problem:

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p$$

Line 4: Definition of the thermal expansivity:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

3.4 Rearrangement of the result given in part (a) produces

$$p + \left(\frac{\partial U}{\partial V}\right)_T = \frac{c_p - c_V}{\alpha V}$$

Taking V to be the given molar volume, this is

$$p + \left(\frac{\partial U}{\partial V}\right)_T = \frac{(45\ \mathrm{J\ K^{-1}\ mol^{-1}})}{(1.24 \times 10^{-3}\ \mathrm{K^{-1}}) \times (88.77 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}})}$$

$$= 4.088 \times 10^8\ \mathrm{Pa}$$

$$= 4036\ \mathrm{atm.}$$

The internal pressure is therefore

$$\left(\frac{\partial U}{\partial V}\right)_T = 4035\ \mathrm{atm.}$$

Physical Chemistry Lecture 4: Summary

The expansions and compressions considered in the last lecture involved gases that were confined in containers with walls that are *diathermal*, *i.e.* allowing the transfer of heat to or from the environment. In this lecture we consider expansions of gases that are thermally isolated - such processes are referred to as *adiabatic*.

The starting point in the analysis of adiabatic processes involving ideal gases is the differential form of the First Law, *viz.*,

$$dU = dq + dw \tag{1}$$

which for an adiabatic process reduces to

$$dU = dw. \tag{2}$$

Recalling the definition of cV and the expression for the differential work increment,

$$c_V dT = -p\, dV \tag{3}$$

and inserting the ideal gas equation on the right hand side we obtain

$$c_V dT = -\frac{RT}{V} dV. \tag{4}$$

To obtain the relationship between temperature and volume, we divide both sides of equation (4) by T and integrate from $T = T_1$, $V = V_1$ to $T = T_2$, $V = V_2$:

$$\int_{T_1}^{T_2} \frac{c_V}{T} dT = -R \int_{V_1}^{V_2} \frac{dV}{V} \tag{5}$$

Assuming that heat capacities are constant, and introducing the formula for the heat capacity difference for an ideal gas,

$$c_V \ln\left(\frac{T_2}{T_1}\right) = -(c_p - c_V) \ln\left(\frac{V_2}{V_1}\right) \tag{6}$$

or

$$\ln\left(\frac{T_2}{T_1}\right) = -(\gamma - 1) \ln\left(\frac{V_2}{V_1}\right), \tag{7}$$

where $\gamma = c_p/c_V$. Finally, we take the exponentials of both sides, and apply the ideal gas law in the form

$$\frac{T_2}{T_1} = \frac{p_2 V_2}{p_1 V_1} \tag{8}$$

to obtain

$$p_1 V_1^{\gamma} = p_2 V_2^{\gamma}. \tag{9}$$

For an irreversible adiabatic expansion, such as would occur if the pressure were suddenly reduced from p_1 to p_2, this result cannot be used. Instead of using the ideal gas law as in equations 4 onwards, the temperature-volume relation is

$$\begin{aligned} c_V(T_2 - T_1) &= -p_2(V_2 - V_1) \\ &= -p_2\left(\frac{RT_2}{p_2} - \frac{RT_1}{p_1}\right). \end{aligned} \tag{10}$$

From this equation, the new temperature can be determined:

$$T_2 = T_1 . \frac{\dfrac{p_2}{p_1} + \dfrac{c_V}{R}}{1 + \dfrac{c_V}{R}}. \tag{11}$$

The mechanical processes of the type considered here and in the previous lecture are of importance in the thermodynamic analysis of heat engines (such as steam engines and internal combustion engines) and refrigeration cycles. The adiabatic gas law is also of importance in acoustics, since the propagation of sound waves through gases involves compressions and rarefactions that are essentially adiabatic. Measurements of the velocity of sound in gases can, in fact, be used to determine the heat capacity ratio and compressibilities.

Learning Objectives

Knowledge

4.1.1 Define the terms 'reversible', 'isothermal', 'adiabatic', 'diathermal'.

Comprehension

4.2.1 Relate the work performed in an adiabatic process to the change in internal energy.

4.2.2 Recognise the path-dependence of work and heat transfers, and the path-independence of the internal energy change.

Application

Calculate:

4.3.1 the heat capacity ratio for a perfect gas, given the constant volume or constant pressure heat capacity.

4.3.2 pressures, temperatures and volumes in reversible adiabatic processes involving perfect gases.

4.3.3 pressures, temperatures and volumes in irreversible adiabatic processes involving perfect gases.

Analysis

4.4.1 Justify steps involved in the derivation of the relation:

$$pV^{\gamma} = \text{constant}$$

Problems

4.1 3.72 mol of a perfect gas, confined to a volume of 10 L at 298 K, expands reversibly and isothermally until its volume has trebled. Calculate the work done, heat transferred and the change in internal energy.
[3.3.1,3.3.3]

4.2 Determine the final pressure of the gas in problem 4.1. Repeat the calculations of w, q and ΔU assuming that the gas is allowed to expand suddenly against this pressure.
[3.3.2,3.3.3]

4.3 Justify each numbered step in the derivation of the adiabatic gas law pV^γ = constant:

$$C_V\, dT = -p\, dV \qquad (1)$$

$$= -\frac{RT}{V} dV \qquad (2)$$

$$\frac{C_V\, dT}{T} = -R\frac{dV}{V}$$

$$c_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V} \qquad (3)$$

$$c_V \ln\left(\frac{T_1}{T_2}\right) = -R \ln\left(\frac{V_2}{V_1}\right) \qquad (4)$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{1-\gamma} \qquad (4)$$

$$\frac{p_2V_2}{p_1V_1} = \left(\frac{V_2}{V_1}\right)^{1-\gamma} \qquad (5)$$

$$p_2V_2^\gamma = p_1V_1^\gamma$$

[4.4.1]

4.4 Calculate the heat capacity ratio, $\gamma = c_p/c_V$, for a perfect monatomic gas with $c_V = 3R/2$.
[4.3.1]

4.5 1.23 mol of the gas of problem 4.4 expands reversibly and adiabatically from V_1 = 15.82 L at T_1 = 300 K until its volume has doubled. Calculate the final pressure of the gas and its internal energy change.
[4.3.2]

4.6 One mole of perfect gas at temperature T_1, volume V_1 and pressure p_1 absorbs heat q_V at constant volume. Assuming that c_V is constant, derive expressions for the final temperature T_2 and pressure p_2, and the internal energy change ΔU for the process.
[3.3.1,3.3.3]

4.7 Suppose that the gas in problem 4.6 expands isothermally and reversibly at T_2 to pressure p_1.

(i) Determine the final volume V_2.

(ii) Determine the internal energy change for the process (p_2, V_1, T_2) -> (p_1, V_2, T_2).
[3.3.1]

(iii) Compare the total heat absorbed by the gas in the composite process (p_1, V_1, T_1) -> (p_2, V_1, T_2) -> (p_1, V_2, T_2) with the heat that would be absorbed in the direct process (p_1, V_1, T_1) -> (p_1, V_2, T_2). What do you notice? [1.2.5, 1.1.1(xii)]

Solutions

4.1 Given $n = 3.712$ mol, $T = 298$ K, $V_1 = 10$ L. The volume trebles, so $V_2 = 30$ L. Since the expansion is reversible, the ideal gas law is obeyed at each intermediate volume. Therefore,

$$
\begin{aligned}
w &= -\int_{V_1}^{V_2} p\, dV \\
&= -nRT \int_{V_1}^{V_2} \frac{dV}{V} \\
&= -nRT \ln\left(\frac{V_2}{V_1}\right)
\end{aligned}
$$

$$= -(3.72\text{ mol}) \times (8.314\text{ J K}^{-1}\text{ mol}^{-1}) \times (298\text{ K}) \times \ln 3$$

$$= -10.12\text{ kJ}$$

Since the internal energy of a perfect gas depends only on temperature, the internal energy change is zero, so by the First Law,

$$q = -w = 10.12\text{ kJ}.$$

4.2 The final pressure is

$$p = \frac{nRT}{V} = \frac{(3.27\text{ mol}) \times (8.314\text{ J K}^{-1}\text{ mol}^{-1}) \times (298\text{ K})}{(3.00 \times 10^{-2}\text{ m}^3)}$$

$$= 2.70 \times 10^5\text{ Pa}.$$

The work involved in expanding irreversibly against this constant pressure is

$$
\begin{aligned}
w &= -p\,(V_2 - V_1) \\
&= -(2.70 \times 10^5\text{ Pa}) \times (2.00 \times 10^{-2}\text{ m}^3) \\
&= -5.40\text{ kJ}.
\end{aligned}
$$

As before, the internal energy change is zero, so the heat absorbed is $q = 5.40$ kJ.

4.3 Step 1: follows from the differential form of the first law, *viz.*

$$dU = dq + dw$$

with $dq = 0$.
Step 2: the ideal gas law is assumed.
Step 3: the heat capacity is assumed to be independent of temperature.
Step 4: heat capacity ratio is introduced, along with the result

$$c_p - c_V = R$$

Step 5: ideal gas law is used in the form

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

4.4 Since $c_p - c_V = R$ we have

$$\begin{aligned} c_p &= c_V + R \\ &= (1 + \frac{3}{2})R \\ &= \frac{5}{2}R \end{aligned}$$

Therefore $c_p/c_V = 5/3$.

4.5 The initial pressure is required if we want to use the result pV^γ = constant. This pressure is

$$\begin{aligned} p_1 = \frac{n_1RT_1}{V_1} &= \frac{(1.23\ \mathrm{mol}) \times (8.314\ \mathrm{J\ K^{-1}mol^{-1}}) \times (300\ \mathrm{K})}{(1.582 \times 10^{-2}\ \mathrm{m^3})} \\ &= 1.939 \times 10^5\ \mathrm{Pa}. \end{aligned}$$

$$p_1V_1^\gamma = p_2V_2^\gamma$$

$$\begin{aligned} p_2 = p_1(\frac{V_1}{V_2})^\gamma &= (1.939 \times 10^5\ \mathrm{Pa}) \times (\frac{1}{2})^{5/3} \\ &= 6.107 \times 10^4\ \mathrm{Pa}. \end{aligned}$$

The temperature corresponding to this pressure is

$$\begin{aligned} T_2 &= \frac{p_2V_2}{nR} \\ &= \frac{(6.107 \times 10^4\ \mathrm{Pa}) \times (3.164 \times 10^{-2}\ \mathrm{m^3})}{(1.23\ \mathrm{mol}) \times (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})} \\ &= 189.0\ \mathrm{K}. \end{aligned}$$

The internal energy change is therefore

$$\begin{aligned} \Delta U &= nc_V(T_2 - T_1) \\ &= (1.23\ \mathrm{mol}) \times (1.5 \times 8.314\ \mathrm{J\ K^{-1}mol^{-1}}) \times (189.0 - 300) \\ &= -\ 1.703\ \mathrm{kJ}. \end{aligned}$$

4.6 The temperature rise satisfies

$$\begin{aligned} q_V &= c_V(T_2 - T_1) \\ T_2 &= T_1 + \frac{q_V}{c_V} \\ &= T_1(1 + \frac{q_V}{c_VT_1}). \end{aligned}$$

Since the ideal gas law holds, we must also have

$$\frac{p_2}{p_1} = \frac{T_2}{T_1} = 1 + \frac{q_V}{c_V T_1}$$

so that

$$p_2 = p_1(1 + \frac{q_V}{c_V T_1}).$$

Also, by definition, the internal energy change is equal to q_V.

4.7(i) The final volume V_2 is determined from Boyle's law in the form

$$\begin{aligned} V_2 &= V_1 \frac{p_2}{p_1} \\ &= V_1[1 + \frac{q_V}{c_V T_1}]. \end{aligned}$$

(ii) The internal energy change for the isothermal process at temperature T_2 is zero.

(iii) The total heat absorbed in the composite process is

$$\begin{aligned} q_{total} &= c_V(T_2 - T_1) + RT_2 \ln (\frac{V_2}{V_1}) \\ &= c_V(T_2 - T_1) + RT_2 \ln (1 + \frac{q_V}{c_V T_1}). \end{aligned}$$

This is to be compared with the heat absorbed in the expansion from (V_1, T_1) to (V_2, T_2) at constant pressure p_1, which is

$$\begin{aligned} q_p &= \Delta H \\ &= c_p(T_2 - T_1). \end{aligned}$$

Recalling the relation between c_p, c_V and R, and applying the ideal gas law, this quantity can also be expressed as

$$\begin{aligned} q_p &= c_V(T_2 - T_1) + R(T_2 - T_1) \\ &= c_V(T_2 - T_1) + p_1(V_2 - V_1). \end{aligned}$$

These two heats are not the same, whicih illustrates the fact that q is not a function of state.

Physical Chemistry Lecture 5: Summary

In the previous lecture we considered the work and internal energy changes associated with adiabatic compression and expansion of perfect gases. Another type of adiabatic process that is of interest is the adiabatic expansion of a gas through a throttle valve or nozzle, resulting in a decrease in pressure. The great practical importance of such processes is that the temperature of the gas can also decrease. This phenomenon is known as the *Joule-Thomson effect.* To analyse the Joule-Thomson effect by application of the First Law, consider a fixed quantity of gas occupying volume V_i at the initial high pressure p_i, and V_f at the lower pressure p_f. The work required to force the gas through the nozzle is

$$\begin{aligned} w &= p_iV_i - p_fV_f \\ &= \Delta U, \end{aligned} \tag{1}$$

since the process is adiabatic ($q = 0$). This work must be done against the cohesive forces of the fluid. Equation 1 can be rearranged to give

$$\Delta U + p_fV_f - p_iV_i = \Delta U + \Delta(pV) = 0 \tag{2}$$

which shows that the enthalpy is constant, *i.e.*, the throttling process is therefore *isenthalpic.* It is of interest to determine how the temperature varies with pressure in the process. This relationship can be determined by considering the differential of H as a function of temperature and pressure, *viz.*,

$$dH = \left(\frac{\partial H}{\partial T}\right)_p dT + \left(\frac{\partial H}{\partial p}\right)_T dp \tag{4}$$

and setting $dH = 0$ (imposing the condition of constant enthalpy). This results in the relation

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p} \tag{5}$$

where the quantities

$$\left(\frac{\partial T}{\partial p}\right)_H \quad \text{and} \quad \left(\frac{\partial H}{\partial p}\right)_T$$

are referred to respectively as the *Isenthalpic* and *Isothermal Joule-Thomson Coefficients.* The isenthalpic Joule-Thomson coefficient is readily measurable, with a typical value of 0.1 - 1 K/atm, and is known to be a function of temperature and pressure. The temperature change in a gas undergoing an isenthalpic expansion between pressures p_1 and p_2 is given by

$$\Delta T = \int_{p_1}^{p_2} \left(\frac{\partial T}{\partial p}\right)_H dp \tag{6}$$

from which it is seen that if $p_1 > p_2$, the Joule-Thomson coefficient must be positive to result in a decrease in the temperature. The coefficient changes sign at the *Joule-Thomson inversion point,* which also depends on the pressure and temperature. For hydrogen and helium, the Joule-Thomson coefficient is negative under most practically-important conditions.

The Joule-Thomson effect is of crucial importance in the liquefaction of gases. The gas to be liquefied is compressed and driven through a throttle valve, during which its temperature decreases (if it is beneath the inversion temperature). This cooled gas is passed through a counter-current heat exchanger, which lowers the temperature of gas about to undergo the throttling process. The temperature of the gas thereby becomes progressively lower, until it eventually liquefies.

In addition to being used in the production of liquid air and related products, the Joule-Thomson effect is even more widely applied in the operation of refrigerators and air conditioners. In a refrigerator, heat is absorbed by the vaporization of a low-boiling liquid (early models used liquid ammonia or liquid sulphur dioxide, but nowadays chlorofluorocarbons, *e.g.* 'Freon-12' are used). The heat absorbed by the fluid is given up to the environment through an external heat-exchanger. To function continuously, the vaporized refrigerant must be returned to the liquid state; this is achieved by the Joule-Thomson effect.

As we have observed, the Joule-Thomson effect originates from the existence of cohesive forces in the gas. Another manifestation of these forces is in the variation of enthalpy with temperature at constant volume. This can be determined from equation 1: dividing by dT and imposing the condition of constant V, we obtain

$$\begin{aligned}\left(\frac{\partial H}{\partial T}\right)_V &= \left(\frac{\partial H}{\partial T}\right)_p + \left(\frac{\partial H}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V \qquad (7)\\ &= c_p\left[1 - \frac{\alpha}{\beta}\left(\frac{\partial T}{\partial p}\right)_H\right]\end{aligned}$$

after application of equation 5 and the definitions of α and β given in earlier lectures.

Learning Objectives

Knowledge

5.1.1 Define the terms 'Joule-Thomson coefficient', 'isenthalpic', 'Joule-Thomson inversion temperature'.

Comprehension

5.2.1 Demonstrate the constancy of enthalpy in an adiabatic throttling process.

5.2.2 Relate the decrease in temperature to the existence of cohesive forces.

Application

Calculate:

5.3.1 Isenthalpic Joule-Thomson Coefficient from Isothermal Joule-Thomson Coefficient and vice versa, given the heat capacity at constant pressure.

5.3.2 temperature change in Joule-Thomson expansion between given pressure limits, assuming constant Joule-Thomson coefficient.

5.3.3 temperature change in Joule-Thomson expansion between given pressure limits, assuming pressure-dependent Joule-Thomson coefficient.

5.3.4 enthalpy of compression from isothermal Joule-Thomson coefficient.

5.3.5 pressure drop required to achieve a given temperature decrease, assuming constant Joule-Thomson coefficient.

5.3.6 pressure drop required to achieve a given temperature decrease, assuming pressure-dependent Joule-Thomson coefficient.

Analysis

Justify the steps involved in the derivation of the relations:

5.4.1

$$\left(\frac{\partial T}{\partial p}\right)_H = -\frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p}$$

5.4.2

$$\left(\frac{\partial H}{\partial T}\right)_V = c_p\left[1 - \frac{\alpha}{\beta}\left(\frac{\partial T}{\partial p}\right)_H\right]$$

Problems

5.1 The average value of the isenthalpic Joule-Thomson coefficient for carbon dioxide at 300 K between 0 atm and 10 atm is 1.09 K atm^{-1}. Estimate the temperature change in an isenthalpic expansion in which pressure is reduced from 10 atm to 1 atm.

[5.3.2]

5.2 The heat capacity of carbon dioxide at 300 K is 37.2 J K^{-1} mol^{-1}. From the Joule-Thompson coefficient given in Problem 5.1, calculate the isothermal Joule-Thomson coefficient, and hence estimate the enthalpy change when 1 mol of carbon dioxide is compressed from 1 to 10 atm at 300 K. How does your value compare with the corresponding enthalpy change for an ideal gas?

[5.3.1,5.3.4]

5.3 The isenthalpic Joule-Thomson coefficient of nitrogen at 298 K between 0 and 140 atm is given by the empirical equation

$$\left(\frac{\partial T}{\partial p}\right)_H = A - Bp, \qquad \text{where } A = 0.2222 \text{ K atm}^{-1} \text{ and} B = 8.0667 \times 10^{-4} \text{ K atm}^{-2}.$$

Calculate the temperature drop when nitrogen undergoes an isenthalpic expansion from 140 atm to 1 atm at 298 K.

[5.3.3]

5.4 A refrigerant has a Joule-Thomson coefficient of 1.35 K atm^{-1} at 20°C. Assuming this to be constant, calculate the pressure drop necessary to produce a temperature decrease of 10°C.

[5.3.5]

5.5 Using the empirical equation for the pressure-dependent Joule-Thomson coefficient for nitrogen given in problem 5.3, calculate the higher pressure p_1 needed to cool the gas by 20 K when it expands to $p_2 = 1$ atm.

[5.3.6]

5.6 The design of the Joule-Thomson experiment arose out of Joule's attempt to determine the internal pressure of a gas from measurement of the change in temperature on expansion of a gas into a vacuum. This is expressed by the partial derivative of T with respect to V at constant U, which is related to c_V and the internal pressure by

$$\left(\frac{\partial U}{\partial V}\right)_V = -c_V\left(\frac{\partial T}{\partial V}\right)_U.$$

(i) Under what circumstances would such a free expansion take place with no change in the internal energy?

(ii) For nitrogen at 298 K and 1 atm, the heat capacities are $c_V = 20.74$ J K^{-1} mol^{-1} and $c_P =$ 29.12 J K^{-1} mol^{-1}, the molar volume is 24.41 L mol^{-1} and the thermal expansivity is 3.671 x 10^{-3} K^{-1}. Use these data to estimate the internal pressure, and the temperature change when a mole of nitrogen doubles its volume at constant U.

Solutions

5.1 Assuming a constant Joule-Thomson coefficient, the temperature and pressure changes are related by

$$\begin{aligned}\Delta T &= \left(\frac{\partial T}{\partial p}\right)_H \Delta p\\ &= (1.09\ \text{K atm}^{-1}) \times (-\ 9\ \text{atm})\\ &= -9.81\ \text{K}.\end{aligned}$$

5.2 The isothermal Joule-Thomson coefficient is

$$\begin{aligned}\left(\frac{\partial H}{\partial p}\right)_T &= -\ c_p \left(\frac{\partial T}{\partial p}\right)_H\\ &= -\ (37.2\ \text{J K}^{-1}\text{mol}^{-1}) \times (1.09\ \text{K atm}^{-1}) \div (1.01325 \times 10^5\ \text{Pa atm}^{-1})\\ &= -\ 4.00 \times 10^{-4}\ \text{m}^3\ \text{mol}^{-1}.\end{aligned}$$

The enthalpy of compression is therefore

$$\begin{aligned}\Delta H &\simeq \left(\frac{\partial H}{\partial p}\right)_T \Delta p\\ &= (-\ 4.00\ \text{m}^3\ \text{mol}^{-1}) \times (9\ \text{atm}) \times (1.01325 \times 10^5\ \text{Pa atm}^{-1})\\ &= -\ 365\ \text{J mol}^{-1}.\end{aligned}$$

For an ideal gas, the corresponding enthalpy of compression is, of course, zero.

5.3 When the Joule-Thomson coefficient depends on pressure, the more general relation for the temperature change is

$$\begin{aligned}\Delta T &= \int_{p_1}^{p_2} \left(\frac{\partial T}{\partial p}\right)_H dp\\ &= \int_{p_1}^{p_2} (A\ -\ Bp)\ dp\\ &= A(p_2\ -\ p_1)\ -\ \frac{1}{2}B(p_2^2\ -\ p_1^2).\end{aligned}$$

Substituting the given values of A and B and the pressure limits,

$$\begin{aligned}\Delta T &= 0.2222 \times (1\ -\ 140)\ -\ \frac{1}{2} \times (8.0667 \times 10^{-4}) \times (1^2\ -\ 140^2)\\ &= -30.89\ +\ 7.90\\ &= -22.99\ \text{K}.\end{aligned}$$

5.4 Assuming a constant Joule-Thomson coefficient, the required pressure change is given by

$$\Delta p = \left(\frac{\partial T}{\partial p}\right)_H^{-1} \Delta T = (10\ \text{K}) \div (1.35\ \text{K atm}^{-1}) = 7.41\ \text{atm}.$$

5.5 After applying the results of problem 5.3, it is seen that the required pressure p_1 is the solution of the quadratic equation

$$\Delta T = Ap_2 - \frac{1}{2}Bp_2^2 - (Ap_1 - \frac{1}{2}Bp_1^2),$$

or

$$-\frac{1}{2}Bp_1^2 + Ap_1 - C = 0$$

where

$$C = Ap_2 - \frac{1}{2}Bp_2^2 - \Delta T = 20.2218$$

using the given values of A, B and p_2. Application of the quadratic formula leads to

$$p_1 = \frac{-A + \sqrt{A^2 + 4(\frac{1}{2}B)(-C)}}{2(-\frac{1}{2}B)}$$

$$= \frac{-0.2222 + 0.1294}{-8.0667 \times 10^{-4}}$$

$$= 115 \text{ atm.}$$

5.6(i) ΔU would be zero if q were zero (achieved by thermal insulation of the whole system) and w were zero (the gas expanded irreversibly against zero pressure).

(ii) Applying earlier results, we have

$$c_p - c_V = [p + (\frac{\partial U}{\partial V})_T]\alpha V,$$

so that

$$(\frac{\partial U}{\partial V})_T = \frac{c_p - c_V}{\alpha V} - p$$

$$= \frac{(8.38 \text{ J K}^{-1}\text{mol}^{-1})}{(3.671 \times 10^{-3} \text{ K}^{-1}) \times (2.441 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1})} - 1.01325 \times 10^5 \text{ Pa}$$

$$= -7.808 \times 10^3 \text{ Pa.}$$

The Joule coefficient is therefore

$$(\frac{\partial T}{\partial V})_U = -\frac{(\frac{\partial U}{\partial V})_T}{(\frac{\partial U}{\partial T})_V}$$

$$= \frac{(7.808 \times 10^3 \text{ Pa})}{(20.74 \text{ J K}^{-1})} = 376 \text{ K m}^{-3},$$

so that

$$\Delta T \simeq (\frac{\partial T}{\partial V})_U \Delta V = (376 \text{ K m}^{-3}) \times (2.441 \times 10^{-2} \text{ m}^3) = 9.18 \text{ K.}$$

Physical Chemistry Lecture 6: Summary

A general feature of thermodynamics is that it does not require any assumptions about the details of molecular and atomic properties or configurations, and can therefore be expected to be universally applicable. Thus, for example, our treatment of work and heat transfers involving gases has not considered the underlying molecular mechanisms of energy absorption. In this lecture, we consider the general problem of how molecules absorb energy, and we examine the implications of a particular model for the distribution of energy in gases.

The absorption of heat by a gas obviously results in an increase in the energy of the molecules. Molecules can absorb energy in various ways that can be identified as follows:

Translational	movement of the centre of mass through space.
Rotational	rotation about the centre of mass.
Vibrational	stretching and bending of bonds.
Electronic	promotion of electrons to molecular orbitals of higher energy.

Clearly, monatomic gases can possess only kinetic (and electronic) energy. While in principle atoms and molecules can absorb energy by undergoing electronic transitions, the energies involved are much larger than those typically encountered in situations where thermodynamics is applied. We can therefore neglect the contribution of electronic transitions to heat capacity.

In the classical-mechanical approximation, description of the state of a molecule requires specification of a number of coordinates, each associated with one of the above kinds of motion or 'mechanical degrees of freedom'. A single atom moving through space can move in three directions, and has three degrees of freedom. A collection of N atoms moving independently has $3N$ degrees of freedom and requires $3N$ coordinates, namely, the velocity components in the x, y, and z directions for each atom. If these N atoms are joined together, they no longer move independently. The system has fewer mechanical degrees of freedom and correspondingly fewer coordinates. The movement of the molecule as a whole can be described by specifying the x, y, and z components of the velocity of the centre of mass, and the three components of the angular momentum about the centre of mass.

There are then $3N - 6$ remaining degrees of freedom and corresponding coordinates to describe the internal motion (*i.e.*, vibration) of the molecule. These coordinates are called the *normal coordinates*. In the special case of a linear molecule, there are only two components of the angular momentum, so that the number of normal coordinates is $3N - 5$ instead of $3N - 6$. Each type of vibration represents a way in which the molecule can absorb energy. As a result, we expect that in general, the larger the molecule, the larger the heat capacity. Calculation of how the contribution of each degree of freedom to the internal energy are determined is a main concern of statistical mechanics, and is beyond the scope of this course. Here, we simply state the most important results of the statistical-mechanical treatment of molecular motion.

(i) The statistical-mechanical treatment of translation yields the result that each component of the centre of mass velocity contributes $RT/2$ to the internal energy and therefore $R/2$ to the heat capacity. The heat capacity of a monatomic perfect gas is thus $3R/2$.

(ii) It can also be shown by statistical mechanics that for nearly all molecules each component of the angular momentum also contributes $R/2$ to the heat capacity.

(iii) The classical-mechanical analysis of molecular vibration is based on a simple model that treats a vibrating bond as two masses connected by as spring. The force required to stretch the spring is proportional to the degree of stretching, and the model is described as a *harmonic oscillator*. According to classical statistical mechanics, each normal vibration contributes R to the heat capacity.

This division of the heat capacity into translational, rotational and vibrational components is called the **Equipartition Theorem**.

For many molecules, substantial discrepancies are observed between experimental heat capacities and those calculated on the basis of the Equipartition Theorem. The most obvious respect in which the theory disagrees with experiment is that it fails to account for the facts that the heat capacity varies markedly with temperature, and that this temperature-dependence differs from molecule to molecule. Even for simple molecules, predicted values of heat capacity at 298 K can be as much as 30 - 50% too low.

The inaccuracy of the Equipartition Theorem can explained by the quantum theory of molecular motion. According to this theory, molecules assume discrete rather than continuous values for their energy. In contrast, the Equipartition Theorem assumes that the molecular energies can assume all values. The accuracy of classical models can be assessed by comparing the spacing between the energy levels with the quantity kT (where k - Boltzmann's constant - is R divided by Avogadro's number). kT is the classical estimate of the average energy of a single harmonic oscillator, and can be regarded as an estimate of the average thermal energy at temperature T.

The spacing between translational energy levels is very much less than kT, so the continuous approximation is very good. The spacing between rotational energy levels is also usually much less than kT for heavy molecules, but can be comparable with, or even greater than kT for light molecules at low temperatures. In contrast, the spacing between vibrational energy levels is nearly always much greater than kT. Consequently, the continuous approximation is reasonable only at high temperatures (usually several thousands of K), and greatly overestimates the vibrational contributions at lower temperatures.

Learning Objectives

Knowledge

6.1.1 Identify components of molecular energy.

6.1.2 Define term 'mechanical degree of freedom'.

Comprehension

6.2.1 Identify various possible degrees of freedom.

Application

Calculate:

6.3.1 Number of mechanical degrees of freedom for linear molecules.

6.3.2 Number of mechanical degrees of freedom for nonlinear molecules.

6.3.3 Heat capacities and heat capacity ratio by application of Equipartition Theorem.

Analysis

6.4.1 Identify coordinates corresponding to different degrees of freedom.

6.4.2 Give qualitative explanation for the heat-capacity anomaly in terms of quantum theory.

Physical Chemistry Lecture 7: Summary

Thermochemistry is concerned with the application of thermodynamic principles to the study of chemical reactions. In this and the next few lectures we shall illustrate various ways in which the First Law of Thermodynamics can be applied. In particular, we shall be concerned with estimation of enthalpy and internal energy changes for chemical reactions that cannot be studied experimentally, either because they simply do not occur or because they proceed too slowly to produce a satisfactorily measurable enthalpy change.

Chemical reactions are most often characterised thermodynamically in terms of their enthalpy change. Reactions for which ΔH is negative (heat is given out) are said to be *exothermic*, while reactions for which ΔH is positive (heat is absorbed) are said to be *endothermic*. Thermochemical analyses depend ultimately on the availability of accurate measurements of enthalpy changes. For some reactions these can be determined by *calorimetry*, which in its simplest form involves measuring the temperature rise caused by a chemical reaction carried out in an apparatus of known heat capacity. The heat capacity of a calorimeter is determined by measuring the temperature rise due to a precisely-known heat input, usually produced by passing an electric current through a resistance.

The accuracy of a calorimetric measurement depends on how successfully heat losses to the environment are eliminated. The elimination of such losses is much easier to achieve by use of a closed, constant-volume reaction vessel. The quantity that is measured in such experiments is the heat absorbed or evolved at constant volume, which is proportional to the internal energy change, ΔU. The heat evolved or absorbed is proportional to ΔH only in calorimetric measurements at constant pressure, which are, however, much more difficult.

The relation between ΔU and ΔH involves the volume change for the reaction:

$$\Delta H = \Delta U + \Delta(pV) \qquad (1)$$

For reactions occurring in condensed phases the 'pV' term is nearly always insignificant, so that in these cases there is essentially no difference between the energy and enthalpy changes. For reactions involving gaseous products or reactants, the 'pV' term can be estimated by use of the ideal gas equation (if the pressure is not too great) so that

$$\Delta H = \Delta U + RT\,\Delta n \qquad (2)$$

where Δn is the change in the number of moles of gaseous reactants, as determined from the balanced equation.

Calibration of a calorimeter by use of electrically-generated heat input relies on Joule's expression for the heat evolved by passage of current I through resistance R in time t:

$$q = I^2Rt \qquad (3)$$

If this heat input results in a temperature rise ΔT, the heat capacity C of the calorimeter is given by

$$C = \frac{q}{\Delta T} \qquad (4)$$

Application of the First Law of Thermodynamics to chemical reactions makes use of the fact that the internal energy and enthalpy are functions of state, so that changes in these functions do not depend on intermediate steps. This is expressed as Hess's Law of Constant Heat Summation:

> When initial and final states have different chemical compositions, ΔU and ΔH do not depend on intermediate reactions.

The significance of this result is that an unmeasurable enthalpy change can be expressed as the sum of measurable enthalpy changes. The most important class of reaction to which this is applied is reactions that express the formation of a compound from its component elements. The rules that pertain to the combination of reaction enthalpies are as follows:

1. When an equation is reversed, the sign of ΔH changes.
2. When a reaction is multiplied by a constant, ΔH is also multiplied by the same constant.
3. When identical numbers of moles of a species appear on both sides of an equation, that species can be omitted.

Reaction energy and enthalpy changes are in general dependent on the temperature, as a result of the temperature-dependence of the heat capacities of the reactants and products, and on the states of reactants and products. Thus, energy and enthalpy changes should always be quoted at a particular temperature, and referred to balanced chemical equations showing the state of each participating substance.

To facilitate combination and comparison of enthalpy changes, *standard states* can be defined. The standard state of a substance is that in which it is stable at 298.15 K and 1 bar (where 1 bar = 100 kPa $\simeq$ 1 atm). A *standard enthalpy of reaction* refers to a reaction in which all the reactants are in their standard states.

Learning Objectives

Knowledge

7.1.1 Define the terms 'exothermic', 'endothermic'.

7.1.2 Define the standard state used in reference to enthalpy changes.

7.1.3 State the relation describing the heat evolved by passage of current through a resistor.

Comprehension

7.2.1 Explain the importance of minimising heat losses to the environment in calorimetry.

7.2.2 Describe the procedure for calibration of calorimeters.

Application

Calculate:

7.3.1 the heat evolved by passage of current through a resistor.

7.3.2 heat capacity of calorimeter from heat input and temperature rise.

7.3.3 enthalpy change from heat evolved/absorbed at constant volume.

7.3.4 enthalpy change from combination of intermediate reaction enthalpy changes.

7.3.5 heat evolved/absorbed from molar enthalpy change.

Analysis

7.4.3 Explain the equivalence of Hess's Law and the First Law of Thermodynamics.

Problems

7.1 Calculate the rise in temperature of 253.0 g water (specific heat 4.184 J/g) produced by passage of 0.1032 A through a 100.0 W resistor for 60.00 s, assuming that none of the heat generated is lost to the surroundings.

[7.3.1]

7.2(i) A bomb calorimeter was calibrated by passing a current of 3.212 A through a heater of resistance 10.00 Ω. If the temperature rose by 1.572 °C, calculate the heat capacity of the calorimeter.

[7.2.2,7.3.1,7.3.2]

(ii) When 100g of n-hexane was burned under pressure of oxygen in this calorimeter, the temperature rise was 2.630 °C. Calculate the molar internal energy of combustion, ΔU_c.

(iii) Use your value of ΔU_c to calculate the molar enthalpy of combustion, assuming the validity of the ideal gas equation.

[7.3.3]

7.3(i) For which one of the following reactions

$$\text{n-C}_6\text{H}_{14}(\text{l}) + \frac{19}{2}\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 7\text{H}_2\text{O}(\text{g}) \qquad (1)$$

$$\text{n-C}_6\text{H}_{14}(\text{g}) + \frac{19}{2}\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 7\text{H}_2\text{O}(\text{l}) \qquad (2)$$

$$\text{n-C}_6\text{H}_{14}(\text{l}) + \frac{19}{2}\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 7\text{H}_2\text{O}(\text{l}) \qquad (3)$$

is the enthalpy change the standard enthalpy of combustion of n-hexane?

[7.1.2]

(ii) By addition of the required equations, show how the standard enthalpy of combustion is related to the enthalpy change for the other two reactions.

[7.3.4]

7.4 The enthalpy of vaporization of water at its boiling point (373 K) is 40.71 kJ mol^{-1}. What is the energy required to vaporize 1 kg of water at its boiling point? (Molar mass of water is 18.016 g mol^{-1}).

[7.3.5]

7.5 A room of capacity 75 m^3 at 298 K and 1 atm is to be cooled by an evaporative air cooler. What mass of water must be vaporized to cool the air in this room by 10°C? The enthalpy of vaporization of water at 25°C is 43.8 kJ mol^{-1}, and the heat capacity of air is 21 J K^{-1}mol^{-1}.

[7.3.5]

7.6 A calorimeter devised by Lavoisier and Laplace measured the heat evolved in chemical reactions by the amount of ice melted. Given that the enthalpy of fusion of ice is 6.008 kJ mol^{-1}, calculate the mass of liquid water that would be produced by complete combustion of 3.5 g of graphite:

$$\text{C(gr)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \qquad \Delta H = -\,393.5\ \text{kJ mol}^{-1}$$

assuming no energy losses to the surroundings.

[7.3.5]

7.7 Calculate the standard internal energy of formation (at 298 K and 1 atm pressure) from its standard enthalpy of formation, which is -479.0 kJ mol^{-1}. Other data are as follows:

compound	molar mass/g mol^{-1}	density/g cm^{-3}
$C_4H_8O_2$(l)	88.10	0.900
H_2O(l)	18.02	0.997
CH_3COOH(l)	60.05	1.044
C_2H_5OH(l)	46.07	0.785

Solutions

7.1 The heat evolved by passage of the current is

$$\begin{aligned} q &= I^2Rt \\ &= (0.1032\ \text{A})^2 \times (100.0\ \Omega) \times (60.00\ \text{s}) \\ &= 63.90\ \text{J} \end{aligned}$$

This is related to the temperature change by

$$q = mc\,\Delta T$$

so that

$$\begin{aligned} \Delta T &= \frac{q}{mc} \\ &= \frac{(63.90\ \text{J})}{(253.0\ \text{g}) \times (4.184\ \text{J g}^{-1})} \\ &= 0.06\ \text{K} \end{aligned}$$

7.2(i) If 3.212 A passes through a 10.00 Ω resistor for 28.00 s, the heat generated is

$$\begin{aligned} q_1 &= I^2Rt \\ &= (3.212\ \text{A})^2 \times (10.00\ \Omega) \times (28.00\ \text{s}) \\ &= 2.888\ \text{kJ}. \end{aligned}$$

If this produces a temperature rise of $\Delta T = 1.572$ K, the heat capacity C is

$$\begin{aligned} C &= \frac{q_1}{\Delta T} \\ &= \frac{(2.888\ \text{kJ})}{(1.572\ \text{K})} \\ &= 1.837\ \text{kJ K}^{-1}. \end{aligned}$$

(ii) The temperature rise on combustion of 1.000 g of hexane is 26.24 K. The heat generated is therefore

$$\begin{aligned} q_2 &= C\,\Delta T \\ &= (1.837\ \text{kJ K}^{-1}) \times (26.24\ \text{K}) \\ &= 48.20\ \text{kJ}. \end{aligned}$$

Since the molar mass of hexane is 86.18 g mol^{-1}, the number of mol combusted is

$$n = \frac{(1.000\ \text{g})}{(86.18\ \text{g mol}^{-1})} = 1.160 \times 10^{-2}\ \text{mol}.$$

The molar internal energy of combustion is therefore

$$\begin{aligned}\Delta U_c &= \frac{-q_2}{n}\\ &= \frac{-(48.20\ \text{kJ})}{(1.160\times 10^{-2}\ \text{mol})}\\ &= -4\,155\ \text{kJ mol}^{-1}.\end{aligned}$$

(iii) The relation between the internal energy and enthalpy changes is

$$\Delta H_c = \Delta U_c + RT\,\Delta n.$$

For the reaction in question, the change in the number of moles in the gas phase is 6 - 19/2 = -7/2 per mole of hexane, so that at 298 K,

$$\begin{aligned}RT\,\Delta n &= (8.314\ \text{J K}^{-1}\text{mol}^{-1})\times(298\ \text{K})\times(-3.5\ \text{mol})\\ &= -8.672\ \text{kJ}.\end{aligned}$$

The enthalpy change is therefore

$$\begin{aligned}\Delta H_c &= -4\,155\ \text{kJ mol}^{-1} - 8.672\ \text{kJ mol}^{-1}\\ &= -4\,164\ \text{kJ mol}^{-1}.\end{aligned}$$

7.3(i) The enthalpy change of reaction 3 is the standard enthalpy of combustion, since each of the participating substances is in its standard state.

(ii) For reaction 1, the enthalpy change is obtained by adding seven times the enthalpy of vaporization of water to the standard combustion enthalpy:

$$\begin{array}{lll}\mathrm{C_6H_{14}(l)} + \frac{19}{2}\mathrm{O_2(g)} \rightarrow \mathrm{6CO_2(g)} + \mathrm{7H_2O(l)} & & \Delta H = \Delta H_3\\ \qquad\qquad\mathrm{7H_2O(l)} \rightarrow \mathrm{7H_2O(g)} & & \Delta H = 7\Delta H_{vap}(\mathrm{H_2O})\\ \hline \mathrm{C_6H_{14}(l)} + \frac{19}{2}\mathrm{O_2(g)} \rightarrow \mathrm{6CO_2(g)} + \mathrm{7H_2O(l)} & & \Delta H = \Delta H_3 + 7\Delta H_{vap}(\mathrm{H_2O})\end{array}$$

For reaction 2, the enthalpy change is obtained by subtracting the enthalpy of vaporization of hexane:

$$\begin{array}{lll}\mathrm{C_6H_{14}(l)} + \frac{19}{2}\mathrm{O_2(g)} \rightarrow \mathrm{6CO_2(g)} + \mathrm{7H_2O(l)} & & \Delta H = \Delta H_3\\ \mathrm{C_6H_{14}(g)} \qquad\qquad\quad \rightarrow \mathrm{C_6H_{14}(l)} & & \Delta H = -\Delta H_{vap}(\mathrm{C_6H_{14}})\\ \hline \mathrm{C_6H_{14}(g)} + \frac{19}{2}\mathrm{O_2(g)} \rightarrow \mathrm{6CO_2(g)} + \mathrm{7H_2O(l)} & & \Delta H = \Delta H_3 - \Delta H_{vap}(\mathrm{C_6H_{14}})\end{array}$$

7.4 The heat required for vaporization of 1 kg of water is

$$\begin{aligned} q &= n\,\Delta H_{vap} \\ &= \frac{(1000.0\ \text{g kg}^{-1})}{(18.02\ \text{g mol}^{-1})} \times (40.71\ \text{kJ mol}^{-1}) \\ &= 2.259\ \text{MJ kg}^{-1} \end{aligned}$$

at the boiling point.

7.5 The number of moles of gas in the room is

$$\begin{aligned} n &= \frac{pV}{RT} \\ &= \frac{(1.013 \times 10^{5}\ \text{Pa}) \times (75\ \text{m}^3)}{(8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (298\ \text{K})} \\ &= 3\,066\ \text{mol}. \end{aligned}$$

The heat removal required to lower the temperature of this quantity of gas is

$$\begin{aligned} q &= nc_p\Delta T \\ &= (3\,066\ \text{mol}) \times (21\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (10\ \text{K}) \\ &= 6.439 \times 10^{5}\ \text{J}. \end{aligned}$$

The number of moles of water that this corresponds to is

$$n_w = \frac{(6.439 \times 10^{5}\ \text{J})}{(43.84 \times 10^{3}\ \text{J mol}^{-1})} = 14.70\ \text{mol}.$$

The mass is therefore

$$(14.70\ \text{mol}) \times (18.02\ \text{g mol}^{-1}) = 265\ \text{g}.$$

7.6 The heat liberated by 3.500g graphite is

$$\begin{aligned} q &= \frac{(3.500\ \text{g})}{(12.011\ \text{g mol}^{-1})} \times (-393.5\ \text{kJ mol}^{-1}) \\ &= -114.7\ \text{kJ}. \end{aligned}$$

The mass of water is therefore

$$\begin{aligned} M &= (18.02\ \text{g mol}^{-1}) \times \frac{(114.7\ \text{kJ})}{(6.008\ \text{kJ mol}^{-1})} \\ &= 344\ \text{g}. \end{aligned}$$

7.7 The molar volumes of the species in the reaction

$$C_2H_5OH(l) + CH_3COOH(l) \rightarrow CH_3COOC_2H_5(l) + H_2O(l)$$

are as follows:

$$C_2H_5OH(l): \quad V_m = \frac{(46.07\ \text{g mol}^{-1})}{(0.785\ \text{g mL}^{-1})} = 58.7\ \text{mL mol}^{-1}$$

$$CH_3COOH(l) \quad V_m = \frac{(60.05\ \text{g mol}^{-1})}{(1.044\ \text{g mL}^{-1})} = 57.5\ \text{mL mol}^{-1}$$

$$CH_3COOC_2H_5(l): \quad V_m = \frac{(88.10\ \text{g mol}^{-1})}{(0.900\ \text{g mL}^{-1})} = 97.9\ \text{mL mol}^{-1}$$

$$H_2O(l): \quad V_m = \frac{(18.02\ \text{g mol}^{-1})}{(0.997\ \text{g mL}^{-1})} = 18.07\ \text{mL mol}^{-1}.$$

The change in volume is therefore

$$\begin{aligned} \Delta V_m &= 18.07 + 97.9 - 57.5 - 58.7 \\ &= -0.23\ \text{mL mol}^{-1}, \end{aligned}$$

so that

$$\begin{aligned} \Delta_f U^\circ &= \Delta_f H^\circ - p\,\Delta V_m \\ &= -479.0\ \text{kJ mol}^{-1} - (1.013 \times 10^5\ \text{Pa}) \times (2.3 \times 10^{-7}\ \text{m}^3\ \text{mol}^{-1}) \\ &= -479.0\ \text{kJ mol}^{-1}, \end{aligned}$$

which is seen to be negligibly different from the given enthalpy of reaction. This is almost always the case for reactions where the reactants and products are in condensed phases.

Physical Chemistry Lecture 8: Summary

In this lecture we illustrate the operation of Hess's Law of Constant Heat Summation by considering the use of enthalpies of combustion (which are usually very large and readily measurable) to estimate the enthalpies of formation for a series of six-carbon cyclic hydrocarbons. This type of calculation is probably the most important use for combustion enthalpy data, since for the vast majority of compounds, enthalpies of formation are not directly measurable. The general procedure involves addition of appropriate multiples of the equations and their corresponding enthalpy changes, according to the rules introduced in the last lecture.

The general procedure can be illustrated for cyclohexene for which the enthalpy of combustion and other relevant data are as follows:

$$C_6H_{10}(l) + \tfrac{17}{2}O_2(g) \rightarrow 6CO_2(g) + 5H_2O(l) \qquad \Delta H_{298} = -3\,747 \text{ kJ}$$
$$C(gr) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H_{298} = -393 \text{ kJ}$$
$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_{298} = -285 \text{ kJ}$$
$$C_6H_{10}(l) \rightarrow C_6H_{10}(g) \qquad \Delta H_{298} = 34 \text{ kJ}$$

(i) To get liquid cyclohexene as the product we need to reverse the combustion reaction:

$$6CO_2(g) + 5H_2O(l) \rightarrow C_6H_{10}(l) + \tfrac{17}{2}O_2(g) \qquad \Delta H_{298} = 3\,747 \text{ kJ}$$

(ii) To ensure the cancellation of six moles of carbon dioxide we multiply the second reaction by 6:

$$6C(gr) + 6O_2(g) \rightarrow 6CO_2(g) \qquad \Delta H_{298} = 6 \times -393 = -2\,358 \text{ kJ}$$

(iii) Likewise, we multiply the third reaction by 5:

$$5H_2(g) + \tfrac{5}{2}O_2(g) \rightarrow 5H_2O(l) \qquad \Delta H_{298} = 5 \times -285 = -1\,425 \text{ kJ}$$

When we add these reactions and their enthalpy changes together, we obtain the enthalpy of formation for cyclohexene in the liquid phase:

$$6C(gr) + 5H_2(g) \rightarrow C_6H_{10}(l)$$
$$\Delta H_{298} = 3\,747 - 2\,358 - 1\,425 = -36 \text{ kJ.}$$

If we want the enthalpy of formation in the gas phase, we have to combine this with the enthalpy of vaporization:

$$6C(gr) + 5H_2(g) \rightarrow C_6H_{10}(l) \qquad \Delta H_{298} = -36 \text{ kJ}$$
$$C_6H_{10}(l) \rightarrow C_6H_{10}(g) \qquad \Delta H_{298} = +34 \text{ kJ}$$

$$6C(gr) + 5H_2(g) \rightarrow C_6H_{10}(g) \qquad \Delta H_{298} = -36 + 34 = -2 \text{ kJ.}$$

The enthalpy of vaporization used in this calculation is that pertaining to 298 K, while the enthalpy of vaporization that is usually tabulated is that at the normal boiling point. As we will see in the next lecture, the difference between these values can be estimated in terms of the heat capacities of the liquid and vapour over this temperature range.

Exactly similar reasoning can be applied to estimate the enthalpy of formation of cyclohexane in the gas phase. The additional thermochemical data that are required here are the enthalpy of combustion

$$C_6H_{12}(l) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H_{298} = -3\,916 \text{ kJ}$$

and the enthalpy of vaporization, which is approximately the same as for cyclohexene:

$$C_6H_{12}(l) \rightarrow C_6H_{12}(g) \qquad \Delta H_{298} = 34 \text{ kJ}$$

The resulting scheme is

$$\begin{array}{lllllll}
6CO_2(g) & + & 6H_2O(l) & \rightarrow & C_6H_{12}(l) & + & 9O_2(g) \quad \Delta H_{298} = 3\,916 \text{ kJ} \\
C_6H_{12}(l) & & & \rightarrow & C_6H_{12}(g) & & \quad \Delta H_{298} = 34 \text{ kJ} \\
6C(gr) & + & 6O_2(g) & \rightarrow & 6CO_2(g) & & \quad \Delta H_{298} = -2\,358 \text{ kJ} \\
6H_2(g) & + & 3O_2(g) & \rightarrow & 6H_2O(l) & & \quad \Delta H_{298} = -1\,710 \text{ kJ} \\
\hline
6C(gr) & + & 6H_2(g) & \rightarrow & C_6H_{12}(g) & & \quad \Delta H_{298} = -118 \text{ kJ.}
\end{array}$$

From the enthalpies of formation of cyclohexane and cyclohexene, the enthalpy of hydrogenation in the gas phase can be estimated:

$$\begin{array}{lllllll}
6C(gr) & + & 6H_2(g) & \rightarrow & C_6H_{12}(g) & & \quad \Delta H_{298} = -118 \text{ kJ} \\
C_6H_{10}(g) & & & \rightarrow & 6C(gr) & + & 5H_2(g) \quad \Delta H_{298} = 2 \text{ kJ} \\
\hline
C_6H_{10}(g) & + & H_2(g) & \rightarrow & C_6H_{12}(g) & & \quad \Delta H_{298} = -116 \text{ kJ.}
\end{array}$$

The operation of Hess's Law is illustrated by direct use of the combustion enthalpies to estimate the enthalpy change for this reaction:

$$\begin{array}{lllllll}
C_6H_{10}(l) & + & \frac{17}{2}O_2(g) & \rightarrow & 6CO_2(g) & + & 5H_2O(l) \quad \Delta H_{298} = -3\,747 \text{ kJ} \\
C_6H_{10}(g) & & & \rightarrow & C_6H_{10}(l) & & \quad \Delta H_{298} = -34 \text{ kJ} \\
6CO_2(g) & + & 6H_2O(l) & \rightarrow & C_6H_{12}(l) & + & 9O_2(g) \quad \Delta H_{298} = 3\,916 \text{ kJ} \\
C_6H_{12}(l) & & & \rightarrow & C_6H_{12}(g) & & \quad \Delta H_{298} = 34 \text{ kJ} \\
H_2(g) & + & \frac{1}{2}O_2(g) & \rightarrow & H_2O(l) & & \quad \Delta H_{298} = -285 \text{ kJ} \\
\hline
C_6H_{10}(g) & + & H_2(g) & \rightarrow & C_6H_{12}(g) & & \quad \Delta H_{298} = -116 \text{ kJ,}
\end{array}$$

which is the same result as obtained less directly from the enthalpies of formation. This means that the set of thermochemical data is internally consistent.

The enthalpies of hydrogenation estimated in either of these ways for the unsaturated hydrocarbons cyclohexene, cyclohexadiene and benzene can be compared by working out the average enthalpy of hydrogenation per double bond. For cyclohexadiene, this average enthalpy is -226/2 = -113 kJ per mole, which is almost the same as the enthalpy of hydrogenation of cyclohexene. For benzene, the average energy per double bond is -204/3 = -68 kJ/mol, which is very different. In other words, if benzene could be regarded as composed of three double bonds equivalent to that in cyclohexene, the heat of hydrogenation would be expected to be 3 x -116 = -348 kJ/mol. The observed difference in enthalpy is called the *resonance energy* and results from electronic stabilization of the benzene molecule. The enthalpy data also show that the enthalpy of hydrogenation of a double bond depends on the molecule in which it is contained; for example, the enthalpy of hydrogenation of cyclohexadiene to cyclohexene is -226 - (-116) = -110 kJ/mol, which is different from the enthalpy of hydrogenation of cyclohexene to cyclohexane.

The enthalpy of the process by which a compound is formed from its elements is a measure of the total energy of all the bonds in the molecule. Crude estimates of enthalpies of formation can therefore be made by adding the enthalpies associated with the various bonds in a molecule. These bond enthalpies can be obtained as average values by applying Hess's Law to the enthalpies of dissociation in the gas phase of molecules that contain only one kind of bond. Thus, by combining the enthalpy of formation of methane with the enthalpy of dissociation of the hydrogen molecule and the enthalpy of sublimation of carbon, the average enthalpy of a single CH bond in methane is esimated to be 416.25 kJ/mol:

$$\begin{array}{llll}
CH_4(g) & \rightarrow & C(gr) + 2H_2(g) & \Delta H_{298} = -(-74.85) = 74.85\ \text{kJ} \\
C(gr) & \rightarrow & C(g) & \Delta H_{298} = 718.38\ \text{kJ} \\
2H_2(g) & \rightarrow & 4H(g) & \Delta H_{298} = 2 \times 435.88 = 871.76\ \text{kJ} \\
\hline
CH_4(g) & \rightarrow & 4H(g) + C(g) & \Delta H_{298} = 1664.99 = 4 \times (416.25\ \text{kJ})
\end{array}$$

Estimation of enthalpies of formation by combination of this value for a CH bond with other bond enthalpies can result in substantial errors (several kJ per bond).

Learning Objectives:

Knowledge

8.1.1 Define standard enthalpy of combustion, resonance energy.

Comprehension

8.2.1 Explain the origin of the difference between enthalpies of reaction involving substances in different states.

8.2.2 Describe how estimates of resonance energy can be made from thermochemical data.

8.2.3 Identify the assumptions inherent in the estimation of enthalpies of formation from individual bond enthalpies

Application

8.3.1 Calculate enthalpies of formation and hydrogenation by addition of reactions and corresponding enthalpy changes

8.3.2 Demonstrate the operation of Hess's Law by calculation of hydrogenation enthalpies from enthalpies of formation and combustion.

8.3.3 Apply Hess's Law to the development of schemes for estimation of bond enthalpies.

8.3.4 Estimate enthalpies of formation from bond enthalpies.

Problems:

8.1 The enthalpy of combustion of ethane to carbon dioxide and water is -1560 kJ mol^{-1}. What is the enthalpy change when 2 mol ethane is formed from its combustion products under the same conditions?

[7.3.5]

8.2(i) From the data for the two isomers of but-2-ene

$$\text{cis-}C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l) \quad \Delta H = -2710 \text{ kJ mol}^{-1}$$

$$\text{trans-}C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l) \quad \Delta H = -2707 \text{ kJ mol}^{-1}$$

calculate the enthalpy of the isomerisation

$$\text{cis-}C_4H_8(g) \rightarrow \text{trans-}C_4H_8(g)$$

(ii) Repeat the above calculation using instead the enthalpies of formation:

$$4C(gr) + 4H_2(g) \rightarrow \text{cis-}C_4H_8(g) \quad \Delta H = -6.99 \text{ kJ mol}^{-1}$$

$$4C(gr) + 4H_2(g) \rightarrow \text{trans-}C_4H_8(g) \quad \Delta H = -11.17 \text{ kJ mol}^{-1}$$

Comment on the likely cause of any discrepancy between the two estimates.

[8.3.1,8.3.2]

Solutions:

8.1 From the given information, the enthalpy of formation of one mole of ethane from its combustion products is +1560 kJ. For 2 moles the enthalpy change is therefore 2 x 1560 kJ = 3120 kJ.

8.2(i) From the combustion reactions

$$\begin{array}{ll}
\text{cis-}C_4H_8(g) + 60_2(g) \rightarrow 4CO_2(g) + 4H_2O(l) & \Delta H = -2710\ \text{kJ} \\
4CO_2(g) + 4H_2O(l) \rightarrow \text{trans-}C_4H_8(g) + 60_2(g) & \Delta H = +2707\ \text{kJ} \\
\hline
\text{cis-}C_4H_8(g) \rightarrow \text{trans-}C_4H_8(g) & \Delta H = -3\ \text{kJ}
\end{array}$$

(ii) From the formation reactions

$$\begin{array}{ll}
4H_2(g) + 4C(gr) \rightarrow \text{trans-}C_4H_8(g) & \Delta H = -11.17\ \text{kJ} \\
\text{cis-}C_4H_8(g) \rightarrow 4H_2(g) + 4C(gr) & \Delta H = -6.99\ \text{kJ} \\
\hline
\text{cis-}C_4H_8(g) \rightarrow \text{trans-}C_4H_8(g) & \Delta H = -4.18\ \text{kJ}
\end{array}$$

The discrepancy is probably due to the large difference in the magnitudes of the formation and combustion enthalpies, and hence in their absolute errors. The combustion enthalpies are quoted to the nearest kJ, while the formation enthalpies are quoted to the nearest 0.01 kJ.

Physical Chemistry Lecture 9: Summary

In the previous lecture we saw how the enthalpy of formation for an organic compound can be estimated from enthalpies of combustion by addition of suitable multiples of reactions and their corresponding enthalpy changes. All the examples we considered can be regarded as applications of a general formula for calculation of enthalpies of formation from enthalpies of combustion:

$$\Delta_f H = -\sum_i \nu_i \Delta_c H_i \qquad (1)$$

where $\Delta_c H_i$ is the combustion enthalpy of compound i, ν_i is the stoichiometric number of compound i (positive for products, negative for reactants), and the summation is over all species in the formation reaction. For example, in the reaction

$$6\mathrm{C(gr)} \ + \ 5\mathrm{H_2(g)} \ \rightarrow \ \mathrm{C_6H_{10}(l)} \qquad (2)$$

we have

$\nu = 1$	$\Delta_c H = -\ 3747$ kJ	for cyclohexene
$\nu = -5$	$\Delta_c H = -285$ kJ	for hydrogen
$\nu = -6$	$\Delta_c H = -393$ kJ	for graphite

so that

$$\Delta_f H = -[1 \times 3\,747 - 6 \times (-393) - 5 \times (-285)] = -36\,\mathrm{kJ}, \qquad (3)$$

as we found previously. From our earlier treatment of this particular reaction, it is clear that the equations that we combined were for reactions involving the formation of each species *from its combustion products*. As we saw earlier by application of Hess's Law, the same result would be obtained if we used reactions involving formation of each species *from its elements*. This procedure is more generally useful, since some substances do not react with oxygen. We can therefore summarise the use of Hess's Law for determining the enthalpy of *any* reaction by the general formula

$$\Delta H = \sum_i \nu_i \Delta_f H_i \qquad (4)$$

where $\Delta_f H_i$ is the enthalpy of formation of compound i. from its elements. The use of this formula requires that all species be in the appropriate states (usually the standard states). The meaning of this equation is that the enthalpy of any reaction is the same as the total enthalpy change involved in decomposing all reactants into their elements and assembling the products from these elements. From this interpretation it is clear that if a species participating in a reaction is an element in its standard state, it will make no contribution to the enthalpy change of such a process. For this reason, we adopt the *convention* that the enthalpy of formation of each element *in its standard state* is assigned the value zero.

In this lecture our primary concern is the thermodynamic treatment of *cyclic* processes, *i.e.*, those in which the starting and finishing states are the same. Since the internal energy and enthalpy depend only on the state of the system, the changes in these functions in cyclic processes are zero. The great importance of such processes lies in the fact that the enthalpy change of one particular step in the cycle can be expressed in terms of the enthalpy changes of all the other steps.

A simple example illustrating the usefulness of thermodynamic cycles is the problem of estimating the enthalpy of vaporization of a liquid at some temperature T lower than the boiling point T_b, given the enthalpy of vaporization ΔH_{vap} at the boiling point and the respective average (constant) heat capacities $c_{p,\mathrm{l}}$ and $c_{p,\mathrm{g}}$ of liquid and vapour over the appropriate temperature range. The steps in the cycle are (i) heat the liquid from T to T_b, (ii) vaporize the liquid at T_b, and (iii) cool the vapour to T.

$$\begin{tikzcd}
\text{Liquid (at } T_b) \arrow[r, "\Delta H_2 = \Delta H_{vap}"'] & \text{Vapour (at } T_b) \arrow[d, "\Delta H_3 = c_{p,g}(T-T_b)"] \\
\text{Liquid (at } T) \arrow[u, "\Delta H_1 = c_{p,1}(T_b-T)"] \arrow[r, "\Delta H = ?"'] & \text{Vapour (at } T)
\end{tikzcd}$$

The sum of all these enthalpy changes is zero, so that

$$\begin{aligned}\Delta H &= \Delta H_1 + \Delta H_2 + \Delta H_3 \\ &= \Delta H_{vap} + (c_{p,1} - c_{p,g})(T_b - T).\end{aligned} \tag{5}$$

Since the heat capacity of a liquid is always greater than that of its vapour, the enthalpy of vaporization at a lower temperature is expected to be greater than at the boiling point. This result is a special case of a general relation that can be derived between the enthalpy change of a chemical reaction at two temperatures T_1 and T_2. The steps in the cycle are essentially the same: (i) heat the reactants from T_1 to T_2, (ii) carry out the reaction at T_2, and (iii) cool the products from T_2 to T_1. If the heat capacities of the species in the reaction are constant, the requirement that all the enthalpy changes cancel out around the cycle yields the result

$$\Delta H(T_2) = \Delta H(T_1) + \Delta c_p(T_2 - T_1) \tag{6}$$

where

$$\Delta c_p = \sum_i \nu_i c_{p,i}$$

is determined by use of the stoichiometric numbers in the same way as implied in equations 1 and 4. In the more general case where the heat capacities of reactants and products depend on temperature,

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta c_p \, dT. \tag{7}$$

A particularly important thermodynamic cycle in which all the steps are chemical reactions is the *Born-Haber Cycle*. This is useful for calculating the lattice enthalpies of ionic solids, *i.e.*, the enthalpy of formation of the solid from its ions in the gas phase. Thus, for example, the lattice enthalpy of the sodium halide NaX

$$\mathrm{Na^+(g)} \quad + \quad \mathrm{X^-(g)} \quad \rightarrow \quad \mathrm{NaX(s)} \qquad \Delta H = \Delta H_{\text{lattice}} \tag{8}$$

can be determined in terms of:

(i) the standard enthalpy of formation of NaX from its elements:

$$\mathrm{Na(s)} \quad + \quad \tfrac{1}{2}\mathrm{X_2(ss)} \quad \rightarrow \quad \mathrm{NaX} \qquad \Delta H = \Delta_f H^{\circ}(\mathrm{NaX})$$

(where ‘ss’ refers to the standard state of the halogen);

(ii) the enthalpy of sublimation of Na:

$$\mathrm{Na(s)} \rightarrow \mathrm{Na(g)} \qquad \Delta H = \Delta H_{\mathrm{sub}}(\mathrm{Na})$$

(iii) the gas-phase ionization enthalpy of Na:

$$\mathrm{Na(g)} \rightarrow \mathrm{Na^+(g)} + \mathrm{e^-(g)} \qquad \Delta H = \Delta H_{\mathrm{ion}}(\mathrm{Na})$$

(iv) the enthalpy of sublimation or vaporization of X_2 from the standard state (this is of course zero for fluorine and chlorine):

$$\tfrac{1}{2}\mathrm{X_2(ss)} \rightarrow \tfrac{1}{2}\mathrm{X_2(g)} \qquad \Delta H = \Delta H_{\mathrm{sub/vap}}(\mathrm{X_2})$$

(v) the enthalpy of dissociation of X_2:

$$\tfrac{1}{2}\mathrm{X_2(g)} \rightarrow \mathrm{X(g)} \qquad \Delta H = \tfrac{1}{2}\Delta H_{\mathrm{diss}}(\mathrm{X_2})$$

(vi) the gas-phase electron affinity of X:

$$\mathrm{X(g)} + \mathrm{e^-(g)} \rightarrow \mathrm{X^-(g)} \qquad \Delta H = \Delta H_{\mathrm{ea}}(\mathrm{X})$$

The Born-Haber cycle incorporating these enthalpy changes is as follows:

$$\begin{tikzcd}
\mathrm{Na^+(g)} + \mathrm{e^-(g)} + \mathrm{X(g)} \arrow[r, "\Delta H = \Delta H_{\mathrm{ea}}(\mathrm{X})"'] & \mathrm{Na^+(g)} + \mathrm{X^-(g)} \arrow[dddd, "\Delta H = \Delta H_{\mathrm{lattice}}"'] \\
\mathrm{Na(g)} + \mathrm{X(g)} \arrow[u, "\Delta H = \Delta H_{\mathrm{ion}}(\mathrm{Na})"'] & \\
\mathrm{Na(s)} + \mathrm{X(g)} \arrow[u, "\Delta H = \Delta H_{\mathrm{sub}}(\mathrm{Na})"'] & \\
\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{X_2(g)} \arrow[u, "\Delta H = \tfrac{1}{2}\Delta H_{\mathrm{diss}}(\mathrm{X_2})"'] & \\
\mathrm{Na(s)} + \tfrac{1}{2}\mathrm{X_2(ss)} \arrow[u, "\Delta H = \tfrac{1}{2}\Delta H_{\mathrm{sub/vap}}(\mathrm{X_2})"'] \arrow[r, "\Delta H = \Delta_f H^{\circ}(\mathrm{NaX})"'] & \mathrm{NaX(s)}
\end{tikzcd}$$

Application of the condition that the enthalpy changes add to zero results in

$$\Delta H_{\mathrm{lattice}} = \Delta_f H^{\circ}(\mathrm{NaX}) - \tfrac{1}{2}\Delta H_{\mathrm{sub/vab}}(\mathrm{X_2}) - \tfrac{1}{2}\Delta H_{\mathrm{diss}}(\mathrm{X_2}) - \Delta H_{\mathrm{sub}}(\mathrm{Na}) - \Delta H_{\mathrm{ion}}(\mathrm{Na}) - \Delta H_{\mathrm{ea}}(\mathrm{X}).$$

Learning Objectives:

Knowledge

9.1.1 State the general formula for the enthalpy of reaction in terms of enthalpies of formation of reactants and products.

9.1.2 State the convention involved in the use of formation enthalpies to calculate enthalpies of reaction.

9.1.3 Define, by use of appropriate balanced chemical equations, the terms 'sublimation enthalpy', 'ionization enthalpy', 'electron affinity', 'lattice enthalpy'.

Comprehension

9.2.1 Give a physical interpretation of the use of formation enthalpies to calculate enthalpies of reaction.

9.2.2 Explain why the overall enthalpy and internal energy changes for cyclic processes are zero.

9.2.3 Describe a thermodynamic cycle that could be used to estimate the effect of temperature on the enthalpy change for a process.

Application

9.3.1 Express the change in a thermodynamic function associated with a chemical reaction in terms of stoichiometric numbers and properties of participating substances.

Calculate

9.3.2 enthalpies of reaction from enthalpies of formation.

9.3.3 enthalpy of vaporization of a liquid at a temperature lower than its boiling point.

9.3.4 enthalpy of reaction at a different temperature, given the value at one temperature and heat capacities (assumed to be constant) of reactants and products.

9.3.5 lattice enthalpies by use of the Born-Haber cycle, given relevant data.

Analysis

9.4.1 Demonstrate the equivalence of the Born-Haber cycle and Hess's Law by appropriate addition of equations and corresponding enthalpy changes.

Problems:

9.1(i) What convention is implied by the expression of an arbitrary enthalpy of reaction in terms of the enthalpies of formation of the reactants and products? [9.1.2]

(ii) Determine the standard enthalpies at 298 K for the following reactions

$$2Na(s) + MgCl_2(s) \rightarrow Mg(s) + 2NaCl(s)$$

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(s)$$

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s)$$

given the standard enthalpies of formation:

	$\Delta_f H^\circ$/kJ mol^{-1}
$MgCl_2(s)$	-641.3
$Al_2O_3(s)$	-1675.7
$NaCl(s)$	-411.2
$Fe_2O_3(s)$	-824.2
$CuSO_4(s)$	-771.4
$CuSO_4.5H_2O(s)$	-2279.7
$H_2O(l)$	-285.8

[9.3.2]

9.2 Construct a thermodynamic cycle to determine the enthalpy of vaporization of water at 298 K, and hence determine the heat absorbed at constant pressure by the vaporization of 1 kg of water at this temperature. You may assume that the heat capacities of steam (33.58 J K^{-1}mol^{-1}) and water (75.29 J K^{-1}mol^{-1}) are constant between 298 and 373 K.

[9.2.3,9.3.3]

9.3 The manufacturers of an evaporative air cooler that uses iced water claim that their device is more efficient (*i.e.*, absorbs significantly more heat for each mass of water vaporized) than other models that use water at 25°C. Use a cycle similar to that developed in Problem 9.2 to compare the enthalpy of vaporization of water at 25°C and 0°C, and hence comment on the manufacturer's claim of greater efficiency.

[9.2.3,9.3.3]

9.4 Devise a thermodynamic cycle to calculate the enthalpy change for the process

$$H_2O(s, 273\ K) \rightarrow H_2O(g, 298\ K)$$

given the following data:

$H_2O(s) \rightarrow H_2O(l)$ $T = 273$ K $\Delta H = 6.011$ kJ mol^{-1}

$H_2O(l) \rightarrow H_2O(g)$ $T = 373$ K $\Delta H = 40.71$ kJ mol^{-1}

$H_2O(l)$ $c_p = 75.29$ J K^{-1}mol^{-1}

$H_2O(g)$ $c_p = 33.58$ J K^{-1} mol^{-1}

[9.2.3,9.3.3]

9.5 Set up an appropriate Born-Haber Cycle and determine the lattice energy of $MgCl_2$ by use of the following data:

$Mg(s) \rightarrow Mg(g)$ $\Delta H = 167.2$ kJ mol^{-1}

$Mg(g) \rightarrow Mg^+(g) + e^-(g)$ $\Delta H = 737.7$ kJ mol^{-1}

$Mg^+(g) \rightarrow Mg^{2+}(g) + e^-(g)$ $\Delta H = 1450.6$ kJ mol^{-1}

$Cl_2(g) \rightarrow 2Cl(g)$ $\Delta H = 241.6$ kJ mol^{-1}

$Cl(g) + e^-(g) \rightarrow Cl^-(g)$ $\Delta H = -364.7$ kJ mol^{-1}

$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$ $\Delta H = -641.3$ kJ mol^{-1}

[9.3.5]

9.6 Given the values of the enthalpy changes for the following reactions involving Na:

$\mathrm{Na(s)} \rightarrow \mathrm{Na(g)}$ $\Delta H = \Delta H_{\mathrm{sub}}(\mathrm{Na})$

$\mathrm{Na(g)} \rightarrow \mathrm{Na^+(g)} + \mathrm{e^-(g)}$ $\Delta H = \Delta H_{\mathrm{ion}}(\mathrm{Na})$

and the halogens (kJ $\mathrm{mol^{-1}}$):

	X=F	Cl	Br	I
$\frac{1}{2}\mathrm{X_2(ss)} \rightarrow \frac{1}{2}\mathrm{X_2(g)}$	0	0	15	31
$\frac{1}{2}\mathrm{X_2(g)} \rightarrow \mathrm{X(g)}$	79	121	97	75
$\mathrm{X(g)} + \mathrm{e^-(g)} \rightarrow \mathrm{X^-(g)}$	-339	-354	-330	-301
$\mathrm{Na(s)} + \frac{1}{2}\mathrm{X_2(ss)} \rightarrow \mathrm{NaX(s)}$	-569	-410	-360	-288

calculate the lattice energies of the four sodium halides.

[9.3.5]

Solutions:

9.1(i) By convention, the enthalpies of formation of the elements in their standard states are zero.

(ii) Use the formula

$$\Delta H^\circ = \sum_i \nu_i \Delta_f H_i^\circ$$

with the convention that the enthalpies of formation of the elements in their standard states are zero. This results in:

(i) $\Delta H^\circ = 2\Delta_f H^\circ(\mathrm{NaCl, s}) - \Delta_f H^\circ(\mathrm{MgCl_2, s})$

$= -822.4 + 641.3$

$= -181.1\ \mathrm{kJ\ mol^{-1}}$

(ii) $\Delta H^\circ = \Delta_f H^\circ(\mathrm{Al_2O_3, s}) - \Delta_f H^\circ(\mathrm{Fe_2O_3, s})$

$= -1675.7 + 824.2$

$= -851.5\ \mathrm{kJ\ mol^{-1}}$

(iii) $\Delta H^\circ = \Delta_f H^\circ(\mathrm{CuSO_4.5H_2O, s}) - 5\Delta_f H^\circ(\mathrm{H_2O, l}) - \Delta_f H^\circ(\mathrm{CuSO_4, s})$

$= -2279.7 + 1429 + 771.4$

$= 79.3\ \mathrm{kJ\ mol^{-1}}$.

9.2 It is required to calculate the enthalpy change for the process

$$\mathrm{H_2O(l, 298\ K)} \rightarrow \mathrm{H_2O(g, 298\ K)}.$$

A thermodynamic cycle that achieves this transformation is

$$\begin{tikzcd}
\mathrm{H_2O(l,\ 373\ K)} \arrow[r, "\Delta H_2"'] & \mathrm{H_2O(g,\ 373\ K)} \arrow[d, "\Delta H_3"] \\
\mathrm{H_2O(l,\ 298\ K)} \arrow[u, "\Delta H_1"] \arrow[r, "\Delta H"'] & \mathrm{H_2O(g,\ 298\ K)}
\end{tikzcd}$$

from which it follows that

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3.$$

The various enthalpy changes are:

$$\begin{aligned}
\Delta H_1 &= c_p \Delta T \\
&= (75.29\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (373\ \mathrm{K} - 298\ \mathrm{K}) \\
&= 5.646\ \mathrm{kJ\ mol^{-1}} \\
\Delta H_2 &= 40.71\ \mathrm{kJ\ mol^{-1}}\ \text{(as given)} \\
\Delta H_3 &= (33.58\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (298\ \mathrm{K} - 373\ \mathrm{K}) \\
&= -2.518\ \mathrm{kJ\ mol^{-1}} \\
\Delta H &= 5.646 + 40.71 - 2.518 \\
&= 43.84\ \mathrm{kJ\ mol^{-1}}.
\end{aligned}$$

Vaporization of the mass of 1 kg will therefore require

$$\begin{aligned}
q &= \frac{(1000\ \mathrm{g\ kg^{-1}})}{(18.02\ \mathrm{g\ mol^{-1}})} \times (43.84\ \mathrm{kJ\ mol^{-1}}) \\
&= 2.430\ \mathrm{MJ\ kg^{-1}}
\end{aligned}$$

at 25°C.

9.3 For evaporation of water at 0°C, the terms in the cycle are

$$\begin{aligned}
\Delta H_1 &= (75.29\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (373\ \mathrm{K} - 273\ \mathrm{K}) \\
&= 7.529\ \mathrm{kJ\ mol^{-1}} \\
\Delta H_2 &= 40.71\ \mathrm{kJ\ mol^{-1}} \\
\Delta H_3 &= (33.58\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (273\ \mathrm{K} - 373\ \mathrm{K}) \\
&= -3.358\ \mathrm{kJ\ mol^{-1}} \\
\Delta H &= 7.529 + 40.71 - 3.358 = 44.88\ \mathrm{kJ\ mol^{-1}}.
\end{aligned}$$

The values for 298 K (43.84 kJ mol^{-1}) and 273 K (44.88 kJ mol^{-1}) differ by only (1.04/43.84) x 100% = 2.4%. The use of chilled water in the cooler appears not to result in substantially greater efficiency (especially when one considers the amount of energy required to chill the water in the first place!).

9.4 The required thermodynamic cycle is

$$\begin{tikzcd}
\mathrm{H_2O(l,\ 373\ K)} \arrow[rr, "\Delta H_3"'] & & \mathrm{H_2O(g,\ 373K)} \arrow[d, "\Delta H_4"] \\
\mathrm{H_2O(l,\ 273\ K)} \arrow[u, "\Delta H_2"] & \mathrm{H_2O(s,\ 273\ K)} \arrow[l, "\Delta H_1"'] \arrow[r, "\Delta H"'] & \mathrm{H_2O(g,\ 298\ K)}
\end{tikzcd}$$

where

$$\begin{aligned}
\Delta H_1 & & &= 6.008\ \mathrm{kJ\ mol^{-1}} \\
\Delta H_2 &= (75.29\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (100\ \mathrm{K}) & &= 7.529\ \mathrm{kJ\ mol^{-1}} \\
\Delta H_3 & & &= 40.71\ \mathrm{kJ\ mol^{-1}} \\
\Delta H_4 &= (33.58\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (75\ \mathrm{K}) & &= \underline{2.519\ \mathrm{kJ\ mol^{-1}}} \\
\Delta H & & &= 56.77\ \mathrm{kJ\ mol^{-1}}.
\end{aligned}$$

9.5 The Born-Haber cycle is

$$\begin{tikzcd}
\mathrm{Mg^{2+}(g) + 2e^-(g) + 2Cl(g)} \arrow[r, "\Delta H_5"] & \mathrm{Mg^{2+}(g) + 2Cl^-(g)} \arrow[dddd, "\Delta H_L"] \\
\mathrm{Mg^+(g) + e^-(g) + 2Cl(g)} \arrow[u, "\Delta H_4"] & \\
\mathrm{Mg(g) + 2Cl(g)} \arrow[u, "\Delta H_3"] & \\
\mathrm{Mg(s) + 2Cl(g)} \arrow[u, "\Delta H_2"] & \\
\mathrm{Mg(s) + Cl_2(g)} \arrow[u, "\Delta H_1"] \arrow[r, "\Delta_f H^o"'] & \mathrm{MgCl_2(s)}
\end{tikzcd}$$

We have $\Delta H_1 = 241.6$, $\Delta H_2 = 167.2$, $\Delta H_3 = 737.7$, $\Delta H_4 = 1450.6$, and $\Delta H_5 = 2 \times (-364.7) = 729.4$ kJ/mol. Therefore

$$\begin{aligned}
\Delta_f H^\circ(\mathrm{MgCl_2}) &= \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_L \\
\Delta H_L &= \Delta_f H^\circ(\mathrm{MgCl_2}) - \Delta H_1 - \Delta H_2 - \Delta H_3 - \Delta H_4 - \Delta H_5 \\
&= -641.3 - 241.6 - 167.2 - 737.7 - 1450.6 - 729.4 \\
&= -3\,967.8 \text{ kJ mol}^{-1}.
\end{aligned}$$

9.6 The Born-Haber Cycle for the calculation of lattice energies of NaX is given in the summary. The numerical results can be determined by application of the resulting formula:

$$\begin{aligned}
\Delta H_{\text{lattice}} = {} & \Delta_f H^\circ(\mathrm{NaX}) - \tfrac{1}{2}\Delta H_{\text{sub/vab}}(\mathrm{X_2}) - \tfrac{1}{2}\Delta H_{\text{diss}}(\mathrm{X_2}) - \Delta H_{\text{sub}}(\mathrm{Na}) \\
& - \Delta H_{\text{ion}}(\mathrm{Na}) - \Delta H_{\text{ea}}(\mathrm{X}).
\end{aligned}$$

For NaF:

$$\begin{aligned}
\Delta H_{\text{lattice}} &= -569 - 0 - 79 - 108 - 502 - (-339) \\
&= -919 \text{ kJ mol}^{-1}.
\end{aligned}$$

For NaCl:

$$\begin{aligned}
\Delta H_{\text{lattice}} &= -410 - 0 - 121 - 108 - 502 - (-354) \\
&= -787 \text{ kJ mol}^{-1}.
\end{aligned}$$

For NaBr:

$$\begin{aligned}
\Delta H_{\text{lattice}} &= -360 - 15 - 97 - 108 - 502 - (-330) \\
&= -752 \text{ kJ mol}^{-1}.
\end{aligned}$$

For NaI:

$$\begin{aligned}
\Delta H_{\text{lattice}} &= -288 - 31 - 75 - 108 - 502 - (-301) \\
&= -703 \text{ kJ mol}^{-1}.
\end{aligned}$$

Physical Chemistry Lecture 10: Summary

In our previous lecture on thermochemistry, we saw how the fact that the change in the thermodynamic functions in cyclic processes is zero allows us to estimate energy changes for processes that cannot be studied directly. In this lecture, we show that consideration of cyclic mechanical processes leads naturally to the introduction of a new thermodynamic function: the entropy.

Cyclic mechanical processes involving expansion and compression of gases have been of interest since the invention of the steam engine over two centuries ago. Even though steam engines are not often used today, cyclic processes are still of great practical significance, since they are ultimately responsible for the operation of all internal combustion engines. The first attempt to develop a theoretical understanding of the operation of the steam engine was made by Carnot, who invented a cycle consisting of four basic steps applied to an ideal gas:

(i) Isothermal expansion at temperature T_h from V_1 to V_2.
(ii) Adiabatic expansion from V_2 to V_3 (T decreases from T_h to T_c).
(iii) Isothermal compression at T_c from V_3 to V_4.
(iv) Adiabatic compression from V_4 to V_1 (T increases from T_c to T_h).

We can apply the First Law of Thermodynamics to each of these steps, as follows:

Step (i):

$$\Delta U = 0, \qquad q = -w = nRT_h \ln(\frac{V_2}{V_1}), \qquad p_1V_1 = p_2V_2 \tag{1}$$

Step (ii):

$$q = 0, \qquad \Delta U = w = nc_V(T_c - T_h), \qquad p_2V_2^\gamma = p_3V_3^\gamma \tag{2}$$

Step (iii):

$$\Delta U = 0, \qquad q = -w = nRT_c \ln(\frac{V_4}{V_3}), \qquad p_3V_3 = p_4V_4 \tag{3}$$

Step (iv):

$$q = 0, \qquad \Delta U = w = nc_V(T_h - T_c), \qquad p_4V_4^\gamma = p_1V_1^\gamma \tag{4}$$

We can derive a relation between the volumes of the gas in the first and last steps by equating the product of the left-hand sides of the 'pV' equations to the products of the right-hand sides:

$$V_1V_2^\gamma V_3V_4^\gamma = V_2V_3^\gamma V_4V_1^\gamma$$

or

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}. \tag{5}$$

With this result, we can connect the amount of heat q_h absorbed at temperature T_h to the amount of heat q_c given out at temperature T_c:

$$q_h = nRT_h \ln(\frac{V_2}{V_1}) \tag{6}$$

$$q_c = -nRT_c \ln(\frac{V_3}{V_4}) = -nRT_c \ln(\frac{V_2}{V_1}). \tag{7}$$

Although these amounts of heat are not equal, it is clear from equations 6 and 7 that if the heat transferred is divided by the *temperature* of the the transfer, the values of the quantity obtained in this way are equal and opposite for the two isothermal steps. In other words, the change in $q(T)/T$ is zero around the cycle:

$$\frac{q_h}{T_h} + \frac{q_c}{T_c} = 0. \tag{8}$$

In general, the heat $q_{rev}(T)$ transferred in a reversible process divided by the temperature T of the process is equal to the change in a function known as the *entropy*, S:

$$\Delta S = \frac{q_{rev}(T)}{T}. \tag{9}$$

The above analysis of the Carnot cycle shows that the overall entropy change for the gas is zero. It can be shown that *any* reversible cyclic mechanical process can be represented by suitable combinations of Carnot cycles, and that the net change in q/T around such a cycle is always zero. We therefore conclude that the entropy is a function of state.

The entropy change for an increase in the volume of an ideal gas is always positive, and can clearly be written in either of the forms

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{p_1}{p_2}\right). \tag{10}$$

which can be obtained by each other by use of the ideal gas equation of state. These results are applicable even if the process is carried out *irreversibly,* since only the initial and final states determine the entropy change. It is also possible to give a molecular interpretation of this entropy change. When the volume increases, we have less information about the position of a particular molecule in the gas. This suggests that an increase in the entropy *of a system* can be associated with a decrease in information about its molecular arrangement.

The definition of the entropy change expressed by equation 9 can also be applied to phase transitions of a pure substance, *e.g.*, fusion or vaporization. The general formula for the entropy of such a phase transition is

$$\Delta S_{tr} = \frac{\Delta H_{tr}}{T_{tr}} \tag{11}$$

where ΔH_{tr} is the enthalpy of transition and T_{tr} is the transition temperature. Reversibility in this context means that the two phases are in equilibrium (*i.e.*, that the transition can proceed in either direction). Since enthalpies of fusion and vaporization are always positive, the corresponding entropy changes are also positive. Again, we can interpret these entropy changes in terms of an decrease in information about the molecular arrangements in the substance, or an increase in the disorder.

It is found that the molar entropy changes for vaporization of nonpolar liquids are fairly similar, with values about 90 J/K/mol; this observation is known as Trouton's Rule. In contrast, the entropies of vaporization for polar substances (such as water and methanol) are significantly higher. This is because strong interactions between molecules tend to result in liquids that have more ordered structures. Since vaporization involves the destruction of this relatively ordered arrangement, we expect the corresponding entropy change to be greater for such substances.

Learning Objectives

Knowledge

10.1.1 Define the entropy change associated with a reversible heat transfer.

Comprehension

10.2.1 Describe the steps involved in the Carnot Cycle, and determine overall changes for the thermodynamic functions.

10.2.2 Give a molecular interpretation for the entropy changes associated with expansion of gases, and with reversible phase transitions.

10.2.3 Interpret deviations from Trouton's Rule observed for polar liquids.

Application

Calculate the entropy changes associated with:

10.3.1 reversible heat transfer at a given temperature.

10.3.2 isothermal changes in the volume or pressure of an ideal gas.

10.3.3 reversible phase transitions (fusion or vaporization) given the appropriate molar enthalpy change and transition temperatures.

10.3.4 cyclic processes applied to a system.

Analysis

10.4.1 Apply the First Law to determine the work and heat transfers in each step of the Carnot Cycle.

10.4.2 Determine the relation between the ideal gas volumes in steps 1 and 3 of the Carnot Cycle.

10.4.3 Demonstrate the constancy of the entropy in the Carnot Cycle.

Problems

10.1 The enthalpy of fusion of CCl_4 at its melting point of 250.3 K is 2.47 kJ mol^{-1}. Calculate the entropy change in 2.35 mol CCl_4 when it melts reversibly at 250.3 K.

[10.3.3]

10.2 Calculate the entropy change experienced by a mole of ideal gas when its pressure doubles isothermally at 298 K. If the process were to take place at a higher temperature, how do you think your result would be affected?

[10.3.2]

10.3 The enthalpy of vaporization of methanol is 38 kJ/mol at its normal boiling point of 64.5^{o}C. Calculate the entropy change in 3.72 mol of methanol vapour when it condenses at this temperature.

[10.3.3]

10.4 A certain machine operates according to a reversible cycle that involves absorption of heat q_1 at temperature T_1 and evolution of heat q_2 at a lower temperature T_2. Derive an expression for the entropy change in the system (*i.e.*, the machine) associated with the other steps in the cycle.

[10.3.4]

Solutions

10.1 The entropy change for reversible fusion is

$$\begin{aligned}\Delta S &= n\frac{\Delta H_{fus}}{T_m}\\ &= (2.35\ \text{mol}) \times \frac{(2.47 \times 10^3\ \text{J mol}^{-1})}{(250.1\ \text{K})}\\ &= 23.2\ \text{J K}^{-1}.\end{aligned}$$

10.2 The entropy change associated with the change in pressure is

$$\Delta S = nR \ln\left(\frac{p_1}{p_2}\right) = -R \ln 2.$$

Since for an ideal gas the temperature dependence of the work and heat of reversible isothermal expansion are given by

$$q = -w = nRT \ln\left(\frac{V_2}{V_1}\right) = nRT \ln\left(\frac{p_1}{p_2}\right)$$

the same will be obtained for the entropy change at any temperature.

10.3 We are given the enthalpy of vaporization, but we are also told that condensation occurs. We therefore expect the enthalpy and entropy changes to be *negative*:

$$\begin{aligned}\Delta S &= \frac{(3.72\ \text{mol}) \times (-\ 38\ \text{kJ mol}^{-1})}{(337.6\ \text{K})}\\ &= -\ 419\ \text{J K}^{-1}.\end{aligned}$$

10.4 Since the cycle is completely reversible and the entropy is a state function, the change in entropy around the cycle is zero. Therefore, the entropy change satisfies

$$\Delta S = \frac{q_1}{T_1} - \frac{q_2}{T_2} + \Delta S_{\text{other steps}} = 0,$$

so that

$$\Delta S_{\text{other steps}} = \frac{q_2}{T_2} - \frac{q_1}{T_1}.$$

Physical Chemistry Lecture 11: Summary

We continue our discussion of the entropy changes of important types of processes by consideration of heating a substance. To derive the entropy change for such a process, suppose that absorption of a small quantity of heat δq_p at constant pressure by a mole of some substance results in the increase of its temperature from T to $T + \delta T$. The relation between the quantity of heat and the temperature change is approximately

$$\delta q_p \simeq c_p \, \delta T \tag{1}$$

for one mole of a substance. Suppose that the temperature changes from T to $T + \delta T$. (The approximate sign is included in equation 1 because in general the heat capacity depends on temperature.) The entropy change caused by the absorption of this quantity of heat is

$$\delta S \simeq \frac{c_p \, \delta T}{T} \tag{2}$$

Taking the limit as δT tends to zero, the total entropy change resulting from change in temperature over some finite temperature range can be obtained by summing all these increments of entropy, which is equivalent to evaluating the integral

$$\Delta S = S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{c_p(T)}{T} \, dT. \tag{3}$$

If the molar heat capacity is constant, as for a monatomic perfect gas, this reduces further to

$$\Delta S = c_p \ln \left(\frac{T_2}{T_1}\right). \tag{4}$$

Since the heat capacity is always positive, it is clear from this equation that the absorption of heat and increase in temperature always correspond to an increase in the entropy. If the temperature decreases, the entropy decreases. The entropy change resulting from heating at constant *volume* is given by the same formulae, but with c_p replaced by c_V.

So far we have concentrated exclusively on calculating the entropy change for a system experiencing various mechanical or thermal processes. In any such process in which the system absorbs heat from or loses heat to the environment, the environment also experiences an entropy change. We can determine this entropy change by assuming that the surroundings act as an infinite reservoir of heat at a given temperature (which remains constant during the process). The entropy change of the environment is therefore given by

$$\Delta S_{env} = \pm \frac{q}{T}, \tag{5}$$

where the positive sign applies if the environment gains heat (*i.e.*, the system loses heat) and the negative sign applies if the environment loses heat (*i.e.*, the system absorbs heat).

As we saw in earlier lectures, the internal energy is the crucial concept which emerges from considering the relation between heat and work, but it must be observed that this provides us with no basis for determining the natural *direction* of processes: it merely states that energy is conserved. The entropy turns out to play a correspondingly significant role in deciding whether such processes are *spontaneous*. However, in contrast to our earlier discussion, we are not interested solely in the changes experienced by the system, but rather in the relation between the entropy changes experienced by the system and by the environment in a given process. The crucial importance of this relation is expressed by the **Second Law of Thermodynamics:**

> "The direction of a spontaneous process is that in which the combined entropy of the system and the environment increases".

$$\Delta S_{sys} + \Delta S_{env} > 0 \tag{6}$$

The First Law of Thermodynamics was arrived at by observation and careful experimentation, and cannot be regarded as being *provable* from first principles. Similar remarks apply to the Second Law; equation (6) merely sums up our extensive experience of natural processes. If a process or machine that violated either of these principles were to be devised, the whole intellectual edifice of thermodynamics would have to be reconstructed.

Much effort has, in fact, been expended in attempting to develop machines that violate the Second Law of Thermodynamics. The most famous of these are known as *perpetual motion machines of the second kind*, which are devices that are supposed to operate in a cyclic process by extracting heat continuously from the environment. The Second Law can be used to understand why such machines won't work. For suppose that such a cycle involved the absorption of heat q from the environment. Since the entropy change experienced by the machine is zero (it operates in a cycle), the combined entropy change for the system (*i.e.*, the machine) and environment is

$$\begin{aligned} \Delta S &= \Delta S_{sys} + \Delta S_{env} \\ &= 0 - \frac{q}{T}; \end{aligned} \tag{7}$$

the only way in which the Second Law can be satisfied is if q is *negative* (*i.e.*, the machine *gives out* heat). This argument is equivalent to an alternative statement of the Second Law, originally made by William Thomson (Lord Kelvin) and Max Planck:

> "It is impossible to construct a cyclic engine that produces no result besides the extraction of heat from a reservoir and its conversion to an equal amount of work."

Consideration of *adiabatic* irreversible processes gives rise to yet another statement of the Second Law. To show this, suppose that an irreversible adiabatic process occurs between two equilibrium states A and B of a system. If the system is restored to its original state A by a *reversible* path, in which heat q_{rev} is transferred from a heat reservoir at temperature T, the overall entropy change for the system in the cycle A -> B -> A is

$$\Delta S_{sys} = S_B - S_A + \frac{q_{rev}}{T} = 0, \tag{8}$$

while that for the environment is

$$\Delta S_{env} = -\frac{q_{rev}}{T}. \tag{9}$$

By the Second Law, this process is possible only if

$$\Delta S_{sys} + \Delta S_{env} = S_B - S_A + \frac{q_{rev}}{T} - \frac{q_{rev}}{T} > 0, \tag{10}$$

so that the adiabatic *irreversible* process A -> B must correspond to an *increase* in the entropy. This leads to an alternative statement of the Second Law:

> "The entropy of an adiabatic system can never decrease."

This statement has profound philosophical implications, for it is our experience of irreversible processes that gives rise to the very concept of time. We also know that irreversible processes do not continue indefinitely. If we regard the universe as an adiabatic system, the point at which all irreversible processes in it have ceased can be regarded as the end of time.

Learning Objectives

Knowledge

11.1.1 State the Second Law of Thermodynamics.

Comprehension

11.2.1 Explain, in terms of the Second Law, the thermodynamic impossibility of perpetual motion machines of the second kind.

Application

Calculate the entropy change

11.3.1 associated with changing the temperature of a system with a constant heat capacity.

11.3.2 associated with changing the temperature of a system with a temperature-dependent heat capacity.

11.3.3 in the environment corresponding to absorption or emission of heat by a system.

Analysis

11.4.1 Prove the equivalence of the Second Law as expressed in terms of entropies of system and environment and the Kelvin-Planck statement.

11.4.2 Use the above statement of the Second Law to show that the entropy increases in an adiabatic irreversible process.

Problems

11.1 The heat capacity of water is 75.29 J K^{-1} mol^{-1}. Assuming this to be constant, calculate the entropy change in 1 kg water when it cools from 100 °C to 25 °C.
[11.3.1]

11.2 The heat capacity c_p of graphite is given by the empirical equation

$$c_p/(\text{J K}^{-1}\text{mol}^{-1}) = a + bT + \frac{c}{T^2}$$

where $a = 16.86$, $b = 4.77 \times 10^{-3}$ K^{-1} and $c = -8.54 \times 10^5$ K^2. Calculate the change in entropy of 5.64 mole graphite when it is heated from 300 K to 400 K.
[11.3.2]

11.3 The heat capacity of copper is $c_p = 24.44$ J K^{-1} mol^{-1} (and assumed to be constant). A block of copper of mass 127 g cools from 400 K to 300 K, and the heat evolved is absorbed by the surroundings at 300 K. Calculate (i) the heat evolved, (ii) the entropy change of the copper, (iii) the entropy change in the surroundings.
[11.3.1,11.3.3]

11.4 Given the standard enthalpies of formation for

$CuSO_4(s)$	- 771.4 kJ mol^{-1}
$CuSO_4.5H_2O(s)$	-2279.7 kJ mol^{-1}
$H_2O(l)$	-285.8 kJ mol^{-1}

calculate the entropy change in the environment when 3.82 mol of anhydrous $CuSO_4$ undergoes the reaction

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s).$$

[11.3.3]

11.5 Given the standard entropies of

$CuSO_4(s)$	109 J K^{-1} mol^{-1}
$CuSO_4.5H_2O(s)$	300.4 J K^{-1} mol^{-1}
$H_2O(l)$	69.91 J K^{-1} mol^{-1}

calculate the standard entropy change for the reaction in Problem 11.4. Use your results to determine whether this process will be spontaneous.

[11.3.3]

11.6 A 1 kg block of Cu (c_p = 24.44 J K^{-1} mol^{-1}) at 200 °C and a 1 kg block of Pb (c_p = 26.44 J K^{-1} mol^{-1}) at 0 °C are placed in thermal contact inside an insulated enclosure. Assuming that the given heat capacities are constant, calculate the entropy change experienced by each block and the entropy change for the isolated system.

[11.3.1]

Solutions

11.1 Assuming a temperature-independent heat capacity, the entropy change per mole is

$$\begin{aligned}\Delta S &= c_p \ln \left(\frac{T_2}{T_1}\right)\\ &= (75.29\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times \ln \left(\frac{373}{298}\right)\\ &= 16.90\ \mathrm{J\ K^{-1}\ mol^{-1}}.\end{aligned}$$

The entropy change for the cooling of 1 kg of water is therefore

$$\frac{(1000\ \mathrm{g})}{(18.02\ \mathrm{g\ mol^{-1}})} \times (16.90\ \mathrm{J\ K^{-1}\ mol^{-1}}) = 937.8\ \mathrm{J\ K^{-1}}.$$

11.2 With the given empirical expression for c_p, the molar entropy change for the graphite is

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_2} \left(a + bT + \frac{c}{T^2}\right) \frac{dT}{T}\\ &= \int_{T_1}^{T_2} \left(\frac{a}{T} + b + \frac{c}{T^3}\right) dT\\ &= a\,[\ln T\,]_{T_1}^{T_2} + b\,[T]_{T_1}^{T_2} + c\left[-\frac{1}{2T^2}\right]_{T_1}^{T_2}\end{aligned}$$

Putting $T_1 = 300$ K and $T_2 = 400$ K,

$$\begin{aligned}\Delta S &= 16.86 \ln \left(\frac{400}{300}\right) + 4.77 \times 10^{-3} \times (400 - 300) - \frac{8.54 \times 10^5}{2} \times \left(\frac{1}{400^2} - \frac{1}{300^2}\right)\\ &= 4.85 + 0.48 + 2.08\\ &= 7.41\ \mathrm{J\ K^{-1}\ mol^{-1}}.\end{aligned}$$

The total entropy change is therefore

$$(5.64\ \mathrm{mol}) \times (7.41\ \mathrm{J\ K^{-1}\ mol^{-1}}) = 41.79\ \mathrm{J\ K^{-1}}.$$

11.3 Assuming a constant heat capacity, the heat evolved is

$$\begin{aligned}q &= nc_p(T_2 - T_1)\\ &= \frac{(127\ \mathrm{g})}{(63.54\ \mathrm{g\ mol^{-1}})} \times (24.44\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (-\,100\ \mathrm{K})\\ &= -\,4.89\ \mathrm{kJ}\end{aligned}$$

(ii) The entropy change of the copper block is

$$\begin{aligned}\Delta S_{sys} &= nc_p \ln\left(\frac{T_2}{T_1}\right)\\ &= (2.00\ \text{mol}) \times (24.44\ \text{J K}^{-1}\ \text{mol}^{-1}) \times \ln\left(\frac{300}{400}\right)\\ &= -14.1\ \text{J K}^{-1}.\end{aligned}$$

(iii) The absorption of heat - q by the environment results in an entropy change of

$$\begin{aligned}\Delta S_{env} &= \frac{-q}{T_{env}}\\ &= \frac{(4.89 \times 10^3\ \text{J})}{(300\ \text{K})}\\ &= 16.3\ \text{J K}^{-1}.\end{aligned}$$

11.4 The standard enthalpy of reaction is

$$\begin{aligned}\Delta H^{o} &= \Delta_f H^{o}(\text{CuSO}_4.5\text{H}_2\text{O, s}) - 5\Delta_f H^{o}(\text{H}_2\text{O, l}) - \Delta_f H^{o}(\text{CuSO}_4\text{, s})\\ &= -2279.7 + 5 \times 285.8 + 771.4\\ &= -79.3\ \text{kJ mol}^{-1}.\end{aligned}$$

The heat generated by reaction of 3.82 mol is therefore

$$\begin{aligned}q_p &= (3.82\ \text{mol}) \times (-79.3\ \text{kJ mol}^{-1})\\ &= -302.9\ \text{kJ}.\end{aligned}$$

Absorption of this quantity of heat by the environment at 298 K results in the entropy change

$$\begin{aligned}\Delta S_{env} &= \frac{-q_p}{T_{env}}\\ &= \frac{(3.029 \times 10^5\ \text{J})}{(298\ \text{K})}\\ &= 1.016 \times 10^3\ \text{J K}^{-1}.\end{aligned}$$

11.5 The standard reaction entropy change is

$$\begin{aligned}\Delta S^{o} &= S^{o}(\text{CuSO}_4.5\text{H}_2\text{O, s}) - 5S^{o}(\text{H}_2\text{O, l}) - S^{o}(\text{CuSO}_4\text{, s})\\ &= 300.4 - 5 \times 69.91 - 109\\ &= -158.2\ \text{J K}^{-1}\ \text{mol}^{-1}.\end{aligned}$$

The entropy change for the system is therefore

$$\Delta S_{sys} = (3.82\ \text{mol}) \times (-158.2\ \text{J K}^{-1}\ \text{mol}^{-1}) = -604.1\ \text{J K}^{-1},$$

so the total entropy change is

$$\begin{array}{ll} \Delta S_{sys} & -604.1 \\ \Delta S_{env} & 1016 \\ \hline \Delta S_{uni} & 412\ \mathrm{J\,K^{-1}}. \end{array}$$

From this result we conclude that the reaction has a tendency to proceed spontaneously (whether it actually does occur depends in general on the kinetics, and cannot be deduced from thermodynamics alone).

11.6 For copper,

$$n_{\mathrm{Cu}} = \frac{(1000\ \mathrm{g})}{(63.54\ \mathrm{g\ mol^{-1}})} = 15.74\ \mathrm{mol}.$$

For lead,

$$n_{\mathrm{Pb}} = \frac{(1000\ \mathrm{g})}{(207.19\ \mathrm{g\ mol^{-1}})} = 4.826\ \mathrm{mol}.$$

We can work out the final temperature of the blocks from the condition that

heat lost by Cu = heat gained by Pb

or

$$-n_{\mathrm{Cu}}c_{p,\mathrm{Cu}}(T - 473.2) = n_{\mathrm{Pb}}c_{p,\mathrm{Pb}}(T - 273.2).$$

Solving for T,

$$T = \frac{473.2 + \dfrac{n_{\mathrm{Pb}}c_{p,\mathrm{Pb}}}{n_{\mathrm{Cu}}c_{p,\mathrm{Cu}}} \times 273.2}{1 + \dfrac{n_{\mathrm{Pb}}c_{p,\mathrm{Pb}}}{n_{\mathrm{Cu}}c_{p,\mathrm{Cu}}}},$$

and since

$$\frac{n_{\mathrm{Pb}}c_{p,\mathrm{Pb}}}{n_{\mathrm{Cu}}c_{p,\mathrm{Cu}}} = \frac{(4.826\ \mathrm{mol}) \times (26.44\ \mathrm{J\,K^{-1}\ mol^{-1}})}{(15.74\ \mathrm{mol}) \times (24.44\ \mathrm{J\,K^{-1}\ mol^{-1}})} = 0.3317,$$

we have

$$T = \frac{473.2 + 0.3317 \times 273.2}{1.3317} = 423.4\ \mathrm{K}.$$

The entropy change for the copper is

$$\Delta S_{\mathrm{Cu}} = n_{\mathrm{Cu}}c_{p,\mathrm{Cu}} \ln \left(\frac{T}{473.2}\right) = (15.74\ \mathrm{mol^{-1}}) \times (24.44\ \mathrm{J\,K^{-1}mol^{-1}}) \times \ln \left(\frac{423.4}{473.2}\right)$$
$$= -42.79\ \mathrm{J\,K^{-1}},$$

while the entropy change for the lead is

$$\Delta S_{\mathrm{Pb}} = n_{\mathrm{Pb}}c_{p,\mathrm{Pb}} \ln \left(\frac{T}{273.2}\right) = (4.826\ \mathrm{mol}) \times (26.44\ \mathrm{J\,K^{-1}mol^{-1}}) \times \ln \left(\frac{423.4}{273.2}\right)$$
$$= 55.90\ \mathrm{J\,K^{-1}}.$$

The entropy change for the isolated system is therefore

$$\Delta S = \Delta S_{\mathrm{Cu}} + \Delta S_{\mathrm{Pb}} = -42.79 + 55.90$$
$$= 13.11\ \mathrm{J\,K^{-1}}.$$

Physical Chemistry Lecture 12: Summary

While the Second Law tells us that natural processes occur in the direction in which the combined entropy of the system and environment increases, it does not specify whether the entropy *increase* of the system is greater in magnitude than the entropy *decrease* of the environment, or *vice versa.* In this lecture, we analyse a variety of processes, which we all know from experience to be irreversible, with the aim of comparing the entropy changes experienced by the system and the environment.

The first such process that we consider is the irreversible cooling of a substance. Since the entropy of the substance (considered as the system) must *decrease*, the entropy *increase* of the environment resulting from the absorption of the heat lost must be of greater magnitude. If the temperature decreases from T_h to T_c and the heat capacity is constant, the heat transferred is

$$q = -c_p(T_h - T_c) \qquad (1)$$

and the entropy changes for the system and environment are

$$\Delta S_{env} = \frac{c_p(T_h - T_c)}{T_c} \quad \text{and} \quad \Delta S_{sys} = -c_p \ln\left(\frac{T_h}{T_c}\right). \qquad (2)$$

We can see that the entropy increase in the environment is always greater than the entropy decrease in the system by observing that

$$\ln\left(\frac{T_h}{T_c}\right) = \ln\left(1 + \frac{T_h - T_c}{T_c}\right) < \frac{T_h - T_c}{T_c}, \qquad (3)$$

for all temperatures$T_h > T_c$ (you can readily verify this inequality by use of a calculator).

The next process we consider is the isothermal expansion of an ideal gas from V_1 to V_2. If this process is carried out reversibly, then as we saw earlier by application of the First Law,

$$q = -w = nRT \ln\left(\frac{V_2}{V_1}\right) \quad \text{so that} \quad \Delta S_{sys} = \frac{q}{T} = nR \ln\left(\frac{V_2}{V_1}\right). \qquad (4)$$

The entropy change in the environment is

$$\Delta S_{env} = -\frac{q}{T} = -nR \ln\left(\frac{V_2}{V_1}\right), \qquad (5)$$

from which it is clear that the entropy changes for the system and environment exactly cancel each other out. When the process is carried out *irreversibly*, application of the First Law gives

$$q = -w = nRT\left(1 - \frac{V_1}{V_2}\right) \quad \text{and again,} \quad \Delta S_{sys} = nR \ln\left(\frac{V_2}{V_1}\right), \qquad (6)$$

since the entropy is a state function: as far as entropy of the system is concerned, it doesn't matter whether the volume changes reversibly or irreversibly. The combined entropy change is therefore

$$\Delta S = -nR\left(1 - \frac{V_1}{V_2}\right) + nR \ln\left(\frac{V_2}{V_1}\right), \qquad (7)$$

and by applying the same properties of the logarithm function as in the first example, we can again show that this expression is always positive. In this case the entropy increase in the system more than compensates for the entropy decrease in the environment.

We finally consider the entropy changes associated with changes of state. A phase change is in general characterised by a transition temperature T_{tr} and molar enthalpy change, and as we saw in our first lecture on entropy, the entropy change for the substance (system) when the phase transition occurs reversibly is obtained by dividing the enthalpy by the transition temperature. Since exactly the same quantity of heat is absorbed from or by the environment at the same temperature, it is easy to see that for a *reversible* phase transition the entropy change in the universe (*i.e.*, the system and environment) is zero:

$$\Delta S_{sys} = \frac{\Delta H_{tr}}{T_{tr}} \qquad \Delta S_{env} = -\frac{\Delta H_{tr}}{T_{tr}} \qquad \Delta S_{uni} = \Delta S_{sys} + \Delta S_{env} = 0 \qquad (8)$$

For an *irreversible* phase transition occurring at some other temperature T, we must include in our calculations the entropy change involved in heating or cooling the product to T from T_{tr}. For example, if a liquid is vaporized at a temperature higher than its boiling point, the heat absorbed from and the entropy change experienced by the environment are

$$q = \Delta H_{vap} + \int_{T_b}^{T} c_{p,g}\, dT \qquad \Delta S_{env} = -\frac{q}{T}, \qquad (9)$$

while the entropy change experienced by the fluid (considered as the system) is

$$\Delta S_{sys} = \frac{\Delta H_{vap}}{T_b} + \int_{T_b}^{T} \frac{c_{p,g}}{T}\, dT. \qquad (10)$$

If the temperature is not very much higher than the boiling point, the terms involving the integrals will make a rather small contribution, and it is easy to see that the entropy increase for the fluid is greater than the entropy decrease for the environment, since

$$\Delta H_{vap}\left(\frac{1}{T_b} - \frac{1}{T}\right) > 0, \qquad (11)$$

whenever $T > T_b$. Similar remarks apply to the freezing of a liquid at a temperature lower than its freezing point, but in this case it can be shown that the entropy increase of the environment is greater.

Learning Objectives

Comprehension

12.2.1 For irreversible processes, determine without calculation whether the entropy change of the system or the environment is greater.

Application

Calculate the entropy changes of the system, the environment and the universe for

12.3.1 cooling of a hot body.

12.3.2 irreversible and reversible isothermal expansion of an ideal gas against constant pressure.

12.3.3 irreversible and reversible vaporization of a liquid or condensation of a vapour.

12.3.4 irreversible or reversible solidification of a liquid or melting of a solid.

12.3.5 any constant-volume process characterized by a given internal energy and entropy changes for the system.

12.3.6 any constant-pressure process characterized by a given enthalpy and entropy changes for the system.

Problems

12.1 3.642 mol of a perfect gas confined to a volume of 10.00 L at 300 K expands irreversibly against a pressure of 1 atm. Calculate the entropy changes for the system, the environment and the universe.
[12.3.2]

12.2 A 1 kg block of ice is removed from a refrigerator and allowed to melt by placing it in contact with surroundings at 300 K. Calculate the entropy changes for the system, the environment and the universe. For ice, the enthalpy of fusion is 6.008 kJ mol^{-1}, and for water $c_p = 75.29$ J K^{-1} mol^{-1}.
[12.3.4]

12.3 58 g of liquid lead at its melting point (600.6 K) is poured into a mould at room temperature. Calculate the entropy change of the lead, the environment and the universe. The enthalpy of fusion of lead is 4.817 kJ mol^{-1}, the heat capacity c_p of solid lead is 26.44 J K^{-1} mol^{-1} and the molar mass is 207.22 g mol^{-1}.
[12.3.4]

12.4 1 m^3 of perfect gas at 273.2 K and 10 atm expands irreversibly against a final pressure of 1 atm. Calculate the entropy changes of the system, the environment and the universe.
[12.3.2]

12.5 Consider a process with an entropy change ΔS and internal energy change ΔU occurring at temperature T in a closed, constant-volume container. What relation must be satisfied by ΔU and ΔS if the process is to proceed spontaneously?
[12.3.5]

12.6 Consider a process with an entropy change ΔS and enthalpy change ΔH occurring at temperature T at constant pressure. What relation must be satisfied by ΔS and ΔH if the process is to proceed spontaneously?
[12.3.6]

Solutions

12.1 The final volume of the gas is

$$\begin{aligned} V_2 &= \frac{nRT}{p_2} \\ &= \frac{(3.642\ \text{mol}) \times (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (300\ \text{K})}{(1.013 \times 10^5\ \text{Pa})} \\ &= 8.967 \times 10^{-2}\ \text{m}^3. \end{aligned}$$

The work done in this irreversible expansion is

$$\begin{aligned} w &= -p_2(V_2 - V_1) \\ &= -(1.013 \times 10^5\ \text{Pa}) \times (8.967 \times 10^{-2}\text{m}^3 - 1.000 \times 10^{-2}\ \text{m}^3) \\ &= -8.070\ \text{kJ}. \end{aligned}$$

Since the gas is perfect, the heat absorbed satisfies

$$\Delta U = q + w = 0$$

$$q = -w = +8.070\ \text{kJ}.$$

The entropy change of the surroundings is

$$\begin{aligned} \Delta S_{env} &= \frac{-q}{T} = \frac{(-8.070 \times 10^3\ \text{J})}{(300\ \text{K})} \\ &= -26.90\ \text{J K}^{-1}, \end{aligned}$$

and the entropy change in the system can be obtained from

$$\begin{aligned} \Delta S_{sys} &= nR\ \ln\left(\frac{V_2}{V_1}\right) \\ &= (3.642\ \text{mol}) \times (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times \ln\left(\frac{8.967 \times 10^{-2}}{1.000 \times 10^{-2}}\right) \\ &= 66.42\ \text{J K}^{-1}. \end{aligned}$$

The entropy change for the universe is therefore

$$\begin{aligned} \Delta S_{uni} &= \Delta S_{env} + \Delta S_{sys} \\ &= -26.90 + 66.42 \\ &= 39.52\ \text{J K}^{-1}. \end{aligned}$$

12.2 The number of moles is

$$n = \frac{(1000\ \text{g})}{(18.02\ \text{g mol}^{-1})} = 55.49\ \text{mol}.$$

The entropy change for the system is

$$\Delta S_{sys} = n[\frac{\Delta H_{fus}}{T_m} + \int_{T_m}^{T} \frac{c_p}{T} dT]$$

$$= (55.49 \text{ mol}) \times [\frac{(6.008 \times 10^3 \text{ J mol}^{-1})}{(273.2 \text{ K})} + (75.29 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln (\frac{300}{273.2})]$$

$$= 1\,611 \text{ J K}^{-1}.$$

The total heat absorbed from the environment is

$$q = n \, \Delta H_{fus} + n \, c_p(T - T_m)$$

$$= (55.49 \text{ mol}) \times [(6.008 \times 10^3 \text{ J mol}^{-1}) + (75.29 \text{ J K}^{-1} \text{ mol}^{-1}) \times (26.8 \text{ K})]$$

$$= 445.4 \text{ kJ},$$

so that the entropy change for the environment is

$$\Delta S_{env} = \frac{-q}{T}$$

$$= \frac{(-4.454 \times 10^5 \text{ J})}{(300 \text{ K})} = -1.485 \times 10^3 \text{ J K}^{-1}.$$

Therefore, the entropy change for the universe is

$$\Delta S_{uni} = \Delta S_{env} + \Delta S_{sys}$$

$$= 1\,611 - 1\,485$$

$$= 126 \text{ J K}^{-1}.$$

12.3 The number of moles is

$$n = \frac{(58 \text{ g})}{(207.2 \text{ g mol}^{-1})} = 0.2799 \text{ mol}.$$

The heat given out in the solidification process is $-\Delta H_{fus}$ per mole, so that

$$q = n \, [-\Delta H_{fus} + c_p(T_2 - T_1)]$$

$$= (0.2799 \text{ mol}) \times [(-4.817 \text{ kJ mol}^{-1}) + (26.44 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.2 \text{ K} - 600.6 \text{ K})]$$

$$= -3.600 \text{ kJ}.$$

The entropy change for the environment resulting from the absorption of this quantity of heat is

$$\Delta S_{env} = \frac{-q}{T_2} = \frac{(3.600 \times 10^3 \text{ J})}{(298.2 \text{ K})}$$

$$= 12.07 \text{ J K}^{-1},$$

while the entropy change for the lead is

$$\Delta S_{sys} = n\,[\frac{-\Delta H_{fus}}{T_1} + c_p \ln (\frac{T_2}{T_1})]$$
$$= (0.2799 \text{ mol}) \times [\frac{(-4.817 \times 10^3 \text{ J mol}^{-1})}{(600.6 \text{ K})} + (26.44 \text{ J K}^{-1}\text{mol}^{-1}) \times \ln (\frac{298.2}{600.6})]$$
$$= -7.426 \text{ J K}^{-1}.$$

The entropy change for the universe is therefore

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{env}$$
$$= 12.07 - 7.426$$
$$= 4.64 \text{ J K}^{-1}.$$

12.4 The number of moles is

$$n = \frac{p_1 V_1}{RT} = \frac{(1.013 \times 10^6 \text{ Pa}) \times (1.000 \text{ m}^3)}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273.2)} = 446.0 \text{ mol},$$

and the final volume is (obviously!) $V_2 = 10\ \text{m}^3$. For the gas,

$$\Delta S_{sys} = nR \ln (\frac{V_2}{V_1}) = (446.0 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times \ln (\frac{10}{1})$$
$$= 8.538 \text{ kJ K}^{-1},$$

and the heat absorbed in the irreversible expansion is

$$q = -w$$
$$= p_2(V_2 - V_1) = (1.013 \times 10^5 \text{ Pa}) \times (9 \text{ m}^3)$$
$$= 9.117 \times 10^5 \text{ J},$$

so that the entropy change for the environment is

$$\Delta S_{env} = \frac{-q}{T} = \frac{(-9.117 \times 10^5 \text{ J})}{(273.2 \text{ K})}$$
$$= -3.337 \text{ kJ K}^{-1}.$$

Therefore,

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{env}$$
$$= 8.538 - 3.337$$
$$= 5.201 \text{ kJ K}^{-1}.$$

12.5 The heat absorbed or evolved at constant volume is by definition equal to the internal energy change ΔU. The entropy change for the environment resulting from this heat transfer is

$$\Delta S_{env} = -\frac{\Delta U}{T},$$

while the entropy change of the system is simply

$$\Delta S_{sys} = \Delta S.$$

The process will occur spontaneously in the direction for which

$$\begin{aligned}\Delta S_{uni} &= \Delta S_{sys} + \Delta S_{env}\\ &= \Delta S - \frac{\Delta U}{T} > 0.\end{aligned}$$

This condition can be written as

$$\Delta A = \Delta U - T\,\Delta S < 0,$$

where A is called the *Helmholtz function.*

12.6 The heat absorbed or evolved at constant pressure is by definition equal to the enthalpy change ΔH. The entropy change for the environment resulting from this heat transfer is

$$\Delta S_{env} = -\frac{\Delta H}{T},$$

while the entropy change of the system is simply

$$\Delta S_{sys} = \Delta S.$$

The process will occur spontaneously in the direction for which

$$\begin{aligned}\Delta S_{uni} &= \Delta S_{sys} + \Delta S_{env}\\ &= \Delta S - \frac{\Delta H}{T} > 0.\end{aligned}$$

This condition can be written as

$$\Delta G = \Delta H - T\,\Delta S < 0,$$

where G is called the *Gibbs function.*

Physical Chemistry Lecture 13: Summary

We observed earlier that the entropy changes corresponding to solid-liquid and liquid-gas transitions are always positive, which suggests that entropy is in some sense a measure of the disorder of molecular arrangements. Our quantitative treatment of entropy has, however, been completely macroscopic, involving the determination of entropy changes by consideration of the amounts of work and heat transferred. To establish a *molecular* interpretation of the entropy, it is necessary to consider not only the spatial distribution of molecules, but also their distribution of energy. This is the concern of *statistical mechanics.*

All the irreversible processes considered have in common a tendency towards a state of *equilibrium*, where no further change occurs. These irreversible changes involve redistribution of molecules among their translational, rotational and vibrational energy levels. The equilibrium state can be characterised not only in terms of an internal energy, but in terms of a quantity known as the *degeneracy*, Ω, which is the number of possible molecular configurations corresponding to the given internal energy. According to statistical mechanics, the equilibrium state corresponds to the *most probable* distribution consistent with the constraints imposed on the system. The entropy is related to the degeneracy by Boltzmann's formula:

$$S = k \ln \Omega = -k \sum_i P_i \ln P_i \tag{1}$$

where P_i is the probability of state i, k is Boltzmann's constant (the gas constant R divided by Avogadro's Number), and summation (or integration) is over all energy levels accessible to the system. When there is only *one* possible configuration, the entropy is zero.

Molecules are distributed among their energy levels by ceaseless vibrations and collisions. As a result, the instantaneous configuration of the system can be expected to fluctuate, but since macroscopic samples of matter contain huge numbers of molecules, fluctuations about the equilibrium value of S and the other thermodynamic functions are extremely small. The most important general conclusion from statistical mechanics is that the distribution of molecules among their energy levels depends strongly on the relative values of individual molecular energies and the quantity kT, which can be regarded as a measure of average thermal energy. When the differences in the molecular energy levels are very small compared to kT (*i.e.*, at high temperatures), we can expect a very broad distribution of molecular energies, which is in turn associated with a large entropy. At very low temperatures, where the energy level differences are very large compared to kT, the populations of the higher molecular energy states will be very small, and the entropy associated with this limiting arrangement is low.

The temperature-dependence of the entropy of a substance can be determined experimentally if the heat-capacity is known as a function of temperature. The general result

$$S(T) - S(T_0) = \int_{T_0}^{T} \frac{c_p(T)}{T}\, dT \tag{2}$$

gives values of entropy at one temperature relative to another: usually the reference temperature is selected to be 0 K. If the interval of integration includes a phase change, the corresponding entropy must also be included. For a gas at temperature T, the relative value of the entropy is

$$S(T) - S(0) =$$

$$\underset{\text{(solid)}}{\int_0^{T_m} \frac{c_{p,\text{solid}}(T)}{T}\, dT} + \underset{\text{(melting)}}{\frac{\Delta H_{fus}}{T_m}} + \underset{\text{(liquid)}}{\int_{T_m}^{T_b} \frac{c_{p,\text{liquid}}(T)}{T}\, dT} + \underset{\text{(boiling)}}{\frac{\Delta H_{vap}}{T_b}} + \underset{\text{(gas)}}{\int_{T_b}^{T} \frac{c_{p,\text{gas}}(T)}{T}\, dT} \tag{3}$$

Heat capacities of substances are known to approach zero as T tends to zero, and it was observed experimentally by Nernst that the entropy change for any process also tends to zero in this limit. This led him to state the Third Law of Thermodynamics:

> "If the entropy of every element in its stable state at 0 K is assigned the value zero, then every substance has a positive entropy which at 0 K may become zero, and does become zero in the case of perfectly crystalline substances".

The association of a perfect crystal with zero entropy can be readily understood from Boltzmann's formula. In a perfect crystal at 0 K, all molecules are in their lowest possible energy states and in a perfectly regular spatial arrangement. There is only one possible configuration for which this is true: $\Omega = 1$, so $S = 0$. The above statement of the Third Law applies only to substances in equilibrium; a glass, for example, may not be in equilibrium because its enormous viscosity causes extremely slow crystallization (which may take centuries). As a result of the irreversibility of all natural processes, it can be shown that it is not possible to reach absolute zero in a finite number of operations (temperatures much lower than a millionth of a degree have, however, been achieved). The impossibility of reaching absolute zero is often taken as a statement of the Third Law.

The Second Law can be used to construct an alternative criterion for spontaneity that incorporates the entropy changes of both the system and the environment. If a process occurs at constant temperature and pressure and involves enthalpy change ΔH and entropy change ΔS, the Second Law requires that

$$\Delta S - \frac{\Delta H}{T} > 0, \qquad \text{or} \qquad \Delta G = \Delta H - T\,\Delta S < 0, \tag{4}$$

where the quantity $G = H - TS$ is called the Gibbs Energy or Gibbs Function. The Gibbs Energy therefore decreases in a spontaneous process. Likewise, application of the Second Law to in constant-volume process at temperature T results in the condition

$$\Delta S - \frac{\Delta U}{T} > 0, \qquad \text{or} \qquad \Delta A = \Delta U - T\,\Delta S < 0, \tag{5}$$

where $A = U - TS$ is known as the Helmholtz Energy or Helmholtz Function. The Gibbs and Helmholtz functions can be related to the maximum work that can be done by the system in a given process. This can be demonstrated starting from a form of the Second Law known as the *Clausius Inequality*:

$$\Delta S \geq \frac{q}{T} \qquad \text{or} \qquad q \leq T\,\Delta S. \tag{6}$$

This result for q can be substituted into the First Law, leading to the inequality

$$\Delta U \leq T\,\Delta S + w \qquad \text{or} \qquad -w \leq -\Delta U + T\,\Delta S; \tag{7}$$

recall that w is *negative* if work is done *by* the system. Taking absolute values of both sides,

$$|w| \leq |\Delta U - T\,\Delta S| = |\Delta A| \tag{8}$$

Since the "=" sign implied here only applies to a reversible process, we can conclude that the maximum possible work obtainable is equal to the change in the Helmholtz Function. At constant pressure, the work done by the system in changing its volume is $-\,p\,\Delta V$. Subtracting this from w and ΔA in equation 8 leads to the result that

$$|w - (-p\,\Delta V)| \leq |\Delta A + p\,\Delta V| = |\Delta G|, \tag{9}$$

which states that the maximum non-pV work that can be obtained from the system is equal to ΔG. An important example of non-pV work is the work associated with driving electrons through the circuit in an electrochemical cell.

Learning Objectives

Knowledge

13.1.1 State the Third Law of Thermodynamics.

13.1.2 Define the configurational degeneracy of a system, and relate this to the entropy by use of Boltzmann's formula.

Comprehension

13.2.1 Describe qualitatively the equilibrium state of a system in terms of the probability of various molecular configurations.

13.2.2 Explain how the entropy of a system depends on the molecular energies relative to kT.

13.2.3 Discuss the significance of the Third Law in terms of Boltzmann's formula.

13.2.4 Describe the variation of heat capacities and entropy changes as temperature approaches absolute zero.

13.2.5 Describe the calculation of Third-Law entropies from heat-capacity variation.

Application

Calculate

13.3.1 the change in Gibbs energy given enthalpy and entropy changes.

13.3.2 the change in Helmholtz energy given internal energy and entropy changes.

13.3.3 the change in entropy over a temperature range that includes a phase transition.

Analysis

13.4.1 Demonstrate the equivalence of the Second Law and the Clausius Inequality.

13.4.2 Demonstrate the equivalence of the Second Law and the conditions $(\Delta G)_{T,p} < 0$ and $(\Delta A)_{T,V} < 0$.

13.4.3 Show how the identification of $|\Delta A|$ as the maximum work obtainable follows from the Clausius Inequality.

13.4.4 Demonstrate the identification of $|\Delta G|$ as the maximum non-pV work obtainable.

Physical Chemistry Lecture 14: Summary

In the last lecture we saw how an irreversible process can be characterised not only in terms of the overall entropy change, but also in terms of changes in the Helmholtz and Gibbs functions, which are in turn related to the maximum work that can be performed by the system in such a process. These new functions are also significant in that they provide a means of predicting the equilibrium state of a system, which is eventually reached when the irreversible process ceases. The Gibbs function proves to be particularly useful in this connexion since, as we saw earlier, it arises naturally from consideration of processes at constant pressure. To predict the position of equilibrium it is first necessary to determine how the Gibbs function depends on pressure and temperature.

The starting point for determining the dependence of A and G on the appropriate independent variables is the combination of the First and Second Laws of Thermodynamics. To do this, suppose that a system changes its volume and temperature by some small but finite amount. Then the change in U is given, for example, by

$$\Delta U = q + w = \int_{T}^{T+\delta T} c_V(T, V + \delta V)\, dT - \int_{V}^{V+\delta V} p(V, T)\, dV. \qquad (1)$$

In the limiting case where the change is carried out reversibly and δT and δV tend to zero, the temperature and pressure are constant and we can express the (infinitesimal) amount of heat absorbed, dq, in terms of the corresponding entropy change, TdS. Thus, we can write

$$\begin{aligned} dU &= dq + dw \\ &= TdS - pdV. \qquad (3) \end{aligned}$$

This important result is called the *Combined First and Second Laws of Thermodynamics*, and is a differential equation expressing the dependence of U on S and V.

To proceed further it is necessary to consider the general relation between changes in *products* like pV and TS and the separate changes in p and V or T and S. If p and V are replaced by $p + \delta p$ and $V + \delta V$ where δp and δV are small but finite changes, the change in pV is

$$\begin{aligned} (p + \delta p)(V + \delta V) - pV &= pV + p\,\delta V + V\,\delta p + \delta p\,\delta V - pV \\ &= p\,\delta V + V\,\delta p + \delta p\,\delta V. \qquad (4) \end{aligned}$$

In the limit as δp and δV tend to zero, the product $\delta p \delta V$ becomes negligible in comparison with the other terms, and we obtain the *differential* of pV, which is written

$$d(pV) = pdV + Vdp. \qquad (5)$$

By use of exactly similar algebra we also obtain the result

$$d(TS) = TdS + SdT. \qquad (6)$$

The differential equations satisfied by each of the functions H, A and G now follow from the definitions of these functions and appropriate combinations of equations 3, 5, and 6:

$$\begin{aligned} dH &= dU + d(pV) &&= TdS + Vdp \qquad (7) \\ dA &= dU - d(TS) &&= -SdT - pdV \qquad (8) \\ dG &= dH - d(TS) &&= Vdp - SdT. \qquad (9) \end{aligned}$$

Since G is a state function, its dependence on p and T can also be expressed in the general form

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT = Vdp - SdT. \qquad (10)$$

These two expressions for dG must be identical, which in turn requires that

$$V = \left(\frac{\partial G}{\partial p}\right)_T \quad \text{and} \quad -S = \left(\frac{\partial G}{\partial T}\right)_p. \qquad (11)$$

The pressure-dependence of G for an ideal gas follows from application of equation 11 to the equation of state: $V = nRT/p$. The quantity of particular importance here is the difference between the Gibbs energy of a gas at some pressure p (expressed in bars) and at a standard pressure p^o (conventionally taken to be 1 bar or 100 kPa).

$$G(T,p) - G(T,p^o) = \int_{p^o}^{p} \frac{nRT}{p}\,dp = nRT \ln\left(\frac{p}{p^o}\right). \qquad (12)$$

Differentiation of this with respect to n gives the *chemical potential*, μ:

$$\mu(T,p) - \mu^o(T,p^o) = \left(\frac{\partial G}{\partial n}\right)_{T,p} - \left(\frac{\partial G}{\partial n}\right)_{T,p^o} = RT \ln\left(\frac{p}{p^o}\right). \qquad (13)$$

where the superscript 'o' is used to refer to the standard state where $p = 1$ bar. For a real gas, the chemical potential is written in terms of the fugacity, f:

$$\mu(T,p) - \mu^o(T,p^o) = RT \ln\left(\frac{f}{p^o}\right) = RT \ln\left(\phi\frac{p}{p^o}\right) \qquad (14)$$

where ϕ is the *fugacity coefficient*, which is always 1 for an ideal gas. This means that the quantity $RT \ln \phi$ is the Gibbs energy difference between the *real gas* at pressure p and the *ideal gas* at pressure p^o at temperature T. For each component i in a mixture of gases, the fugacity is defined in terms of the appropriate *partial pressure*:

$$\mu_i = \mu_i^o + RT \ln\left(\phi_i\frac{p_i}{p^o}\right) = \mu_i^o + RT \ln\left(\phi_i\frac{y_i p}{p^o}\right) \qquad (15)$$

where y_i is the mole fraction, and the fugacity coefficient ϕ_i is again 1 for each component of a mixture of ideal gases.

The great importance of the chemical potential and fugacity is that they allow a general expression to be determined for the equilibrium composition of a mixture undergoing a chemical reaction. This expression is perfectly general and its derivation does not rely on equating the rates of forward and reverse reactions, as is usually the case in elementary treatments. According to the Second Law, the generalised chemical reaction

$$\mathrm{aA + bB \rightarrow cC + dD} \qquad (16)$$

will proceed in the direction in which the total Gibbs function of the system decreases until it reaches equilibrium, at which the Gibbs function is a minimum. At this point, the Gibbs energy of the reactants is equal to the Gibbs energy of the products:

$$\mathrm{a}[\mu_\mathrm{A}^o + RT \ln\left(\frac{f_\mathrm{A}}{p^o}\right)] + \mathrm{b}[\mu_\mathrm{B}^o + RT \ln\left(\frac{f_\mathrm{B}}{p^o}\right)] = \mathrm{c}[\mu_\mathrm{C}^o + RT \ln\left(\frac{f_\mathrm{C}}{p^o}\right)] + \mathrm{d}[\mu_\mathrm{D}^o + RT \ln\left(\frac{f_\mathrm{D}}{p^o}\right)]$$

which can be arranged in the more familiar form

$$\Delta G^{o} = -RT \ln K \qquad (17)$$

where

$$\Delta G^{o} = c\mu^{o}_{C} + d\mu^{o}_{D} - a\mu^{o}_{A} - b\mu^{o}_{B} \qquad \text{and} \qquad K = \frac{\left(\frac{f_C}{p^{o}}\right)^{c}\left(\frac{f_D}{p^{o}}\right)^{d}}{\left(\frac{f_A}{p^{o}}\right)^{a}\left(\frac{f_B}{p^{o}}\right)^{b}}$$

are the *standard Gibbs energy change* and the *equilibrium constant*, respectively. Since the fugacity of each component in general depends on the composition of the mixture, determination of the equilibrium extent of reaction requires numerical solution of equation 17. However, even without doing this it follows that if the standard Gibbs energy change is large and negative, the value of the equilibrium constant will be large and the equilibrium composition will correspond to almost complete conversion of products to reactants.

Learning Objectives

Knowledge

14.1.1 Define the chemical potential in terms of the Gibbs energy and fugacity.

14.1.2 State the condition for chemical reaction equilibrium in terms of the chemical potentials of reactants and products.

Comprehension

14.2.1 Describe how the Combined First and Second Laws equation follows from the general expression for the change in U resulting from finite changes in T and V.

14.2.2 Describe qualitatively the relation between the standard Gibbs energy change at a given temperature, the equilibrium constant, and the extent of reaction.

Application

Calculate

14.3.1 the change in G for an ideal gas resulting from change in the pressure.

14.3.2 the change in G for an incompressible substance resulting from an isothermal change in the pressure.

14.3.3 the contribution of nonideality to the chemical potential of a gas given the value of the fugacity coefficient.

14.3.4 the chemical potential of a component in an ideal gas mixture given its partial pressure or the mole fraction and total pressure.

14.3.5 the standard Gibbs energy change from the equilibrium constant and vice versa.

Analysis

14.4.1 Derive the differential forms for H, A and G from the Combined First and Second Laws and the expressions for $d(pV)$ and $d(TS)$.

14.4.2 Rearrange the condition of chemical equilibrium into the relation $\Delta G^{o} = -RT \ln K$.

Problems

14.1 For lead, the molar mass is 207.2 g mol^{-1} and the normal density is 11.03 g cm^{-1}. Calculate the change in the molar Gibbs energy of lead when the pressure increases by 500 atm, assuming it to be incompressible.

[14.3.2]

14.2 The fugacity coefficient of a certain gas at 300 K and 10 atm pressure is known to be 0.942. Calculate (i) the fugacity and (ii) the nonideal contribution to the chemical potential of the gas under these conditions, assuming a reference pressure of 1 bar.

[14.3.3]

14.3 Calculate the change in the Gibbs energy of 3.265 mol of perfect gas when its pressure increases from 1.013 bar to 5.846 bar at 300 K.

[14.3.1]

14.4 From the following thermochemical data at 298 K

$$3C(gr) + 3H_2(g) \rightarrow \text{cyclo-}C_3H_6(g) \quad \Delta H^o = 53 \text{ kJ mol}^{-1} \quad \Delta G^o = 104 \text{ kJ mol}^{-1}$$

$$3C(gr) + 3H_2(g) \rightarrow CH_3CH{=}CH_2(g) \quad \Delta H^o = 20 \text{ kJ mol}^{-1} \quad \Delta G^o = 62 \text{ kJ mol}^{-1}$$

estimate (i) ΔH^o, (ii) ΔG^o, (iii) ΔS^o, and (iv) the equilibrium constant for the isomerization reaction

$$\text{cyclo-}C_3H_6(g) \rightarrow CH_3CH{=}CH_2(g)$$

[14.3.5]

14.5 Measurements of the equilibrium constants of reactions are often used to determine standard Gibbs energy changes. A relation between the uncertainties in ΔG^o and the equilibrium constant can be determined by differentiating both sides of the equation

$$-\frac{\Delta G^o}{RT} = \ln K$$

with respect to K:

$$\frac{d}{dK}\left(-\frac{\Delta G^o}{RT}\right) = \frac{1}{K}$$

$$\left|\delta\left(\frac{\Delta G^o}{RT}\right)\right| \simeq \frac{\delta K}{K}.$$

(i) Calculate the uncertainty in ΔG^o at 300 K corresponding to a relative error in K of 1%.

(ii) What is the maximum allowable error in K if ΔG^o is required to ± 1 J/mol?

[14.3.5]

14.6 From the following thermochemical data at 298 K for the cis and trans isomers of but-2-ene (in kJ mol^{-1})

$$4C(gr) + 4H_2(g) \rightarrow cis\text{-2-}C_4H_8(g) \quad \Delta H^o = -6.99 \quad \Delta G^o = 65.95$$

$$4C(gr) + 4H_2(g) \rightarrow trans\text{-2-}C_4H_8(g) \quad \Delta H^o = -11.17 \quad \Delta G^o = 63.06$$

estimate (i) ΔH^o, (ii) ΔG^o, (iii) ΔS^o, (iv) the equilibrium constant for the isomerization reaction

$$cis\text{-2-}C_4H_8(g) \rightarrow trans\text{-2-}C_4H_8(g)$$

and (v) the mole fraction of each isomer at equilibrium, assuming a total pressure of 1 bar and that the mixture can be treated as ideal.

[14.3.4,14.3.5]

Solutions

14.1 The molar volume is

$$v = \frac{(207.2\ \mathrm{g\ mol^{-1}})}{(11.03\ \mathrm{g\ mL^{-1}})} = 18.78\ \mathrm{mL\ mol^{-1}} = 1.878 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}.$$

The change in Gibbs energy resulting from the increase in pressure is therefore

$$\begin{aligned}\Delta G &= v\,\Delta p\\ &= (1.878 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}) \times (500 \times 1.013 \times 10^{5}\ \mathrm{Pa}) = 951.2\ \mathrm{J}.\end{aligned}$$

14.2(i) Since the pressure is given in atm and the reference pressure is 1 bar, we need to convert the pressure to bars:

$$p = (10\ \mathrm{atm}) \times (1.013\ \mathrm{bar\ atm^{-1}}) = 10.13\ \mathrm{bar}.$$

The fugacity is therefore

$$f = 0.942 \times (10.13\ \mathrm{bar}) = 9.542\ \mathrm{bar}.$$

(ii) The nonideal contribution to the chemical potential is

$$RT \ln \phi = (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (300\ \mathrm{K}) \times \ln (0.942) = -149.0\ \mathrm{J\ mol^{-1}}.$$

14.3 The increase in Gibbs energy is

$$\begin{aligned}\Delta G &= nRT \ln \left(\frac{p_2}{p_1}\right)\\ &= (3.265\ \mathrm{mol}) \times (8.314\ \mathrm{J\ K^{-1}mol^{-1}}) \times (300\ \mathrm{K}) \times \ln \left(\frac{5.846}{1.013}\right)\\ &= 14.27\ \mathrm{kJ}.\end{aligned}$$

14.4(i) The required standard enthalpy change can be determined by addition of the reactions as follows:

$$\begin{array}{llll}
3\mathrm{C(gr)} + 3\mathrm{H_2(g)} & \rightarrow & \mathrm{CH_3CH{=}CH_2(g)} & \Delta H^{\circ} = 20\ \mathrm{kJ\ mol^{-1}}\\
\text{cyclo-}\mathrm{C_3H_6(g)} & \rightarrow & 3\mathrm{C(gr)} + 3\mathrm{H_2(g)} & \Delta H^{\circ} = -53\ \mathrm{kJ\ mol^{-1}}\\
\hline
\text{cyclo-}\mathrm{C_3H_6(g)} & \rightarrow & \mathrm{CH_3CH{=}CH_2(g)} & \Delta H^{\circ} = -33\ \mathrm{kJ\ mol^{-1}}.
\end{array}$$

(ii) By exactly similar manipulations we find for the corresponding standard Gibbs energy change

$$\Delta G^{\circ} = 62 - 104 = -42\ \mathrm{kJ\ mol^{-1}}.$$

(iii) The entropy change can be determined from the answers to parts (i) and (ii) by rearranging the definition

$$\Delta G^{o} = \Delta H^{o} - T\,\Delta S^{o}$$

into

$$\Delta S^{o} = \frac{\Delta H^{o} - \Delta G^{o}}{T} = \frac{(-33\ \mathrm{kJ\ mol^{-1}}) - (-42\ \mathrm{kJ\ mol^{-1}})}{(298\ \mathrm{K})} = 30\ \mathrm{J\ K^{-1}mol^{-1}}.$$

The fact that this entropy change is positive can be understood in terms of the structural change occurring here: the propene molecule can assume more conformations (*e.g.*, by rotation about the CH_3 - C bond) than the cyclopropane molecule.

(iv) The equilibrium constant is

$$\Delta G^{o} = -RT\ln K \qquad \text{or} \qquad K = \exp(-\frac{\Delta G^{o}}{RT}) = \exp(-\frac{(4.2\times 10^{4}\ \mathrm{J\ mol^{-1}})}{(8.314\ \mathrm{J\ K^{-1}mol^{-1}})\times(298\ \mathrm{K})})$$

$$= 2.3\times 10^{7}.$$

14.5(i) From the given formula it follows that a relative error of 1% (*i.e.*, 0.01) in K at 300 K corresponds to an error in ΔG^{o} of

$$\delta|\Delta G^{o}| \simeq RT\frac{\delta K}{K} = (8.314\ \mathrm{J\ K^{-1}\ mol^{-1}})\times(300\ \mathrm{K})\times(0.01)$$
$$= 25\ \mathrm{J\ mol^{-1}}.$$

(ii) To estimate to within 1 J mol^{-1} we would need to know K with a maximum relative error of

$$\frac{\delta K}{K} = \frac{\delta|\Delta G^{o}|}{RT} = \frac{(1\ \mathrm{J\ mol^{-1}})}{(8.314\ \mathrm{J\ K^{-1}mol^{-1}})\times(300\ \mathrm{K})} = 4\times 10^{-4} = 0.04\%.$$

14.6 Following exactly the same procedure as in Problem 14.4, we find:

(i) the standard enthalpy change:

$$\Delta H^{o} = -11.17 - (-6.99) = -4.18\ \mathrm{kJ\ mol^{-1}}$$

(ii) the standard Gibbs energy change:

$$\Delta G^{o} = 63.06 - 65.95 = -2.89\ \mathrm{kJ\ mol^{-1}}$$

(iii) the standard entropy change:

$$\Delta S^{o} = \frac{\Delta H^{o} - \Delta G^{o}}{T} = \frac{(-4.18\ \mathrm{kJ\ mol^{-1}}) - (-2.89\ \mathrm{kJ\ mol^{-1}})}{(298\ \mathrm{K})} = -4.33\ \mathrm{J\ K^{-1}mol^{-1}}$$

(iv) and the equilibrium constant:

$$K = \exp(-\frac{\Delta G^{o}}{RT}) = \exp(-\frac{(-2.89\times 10^{3}\ \mathrm{J\ mol^{-1}})}{(8.314\ \mathrm{J\ K^{-1}mol^{-1}})\times(298\ \mathrm{K})}) = 3.21.$$

(v) If x is the mole fraction of *trans*-but-2-ene, then

$$K = \frac{x\frac{p}{p^{o}}}{(1-x)\frac{p}{p^{o}}} = \frac{x}{1-x} \qquad \text{or} \qquad x = \frac{K}{K+1} = \frac{3.21}{3.21+1} = 0.762.$$

UNIVERSITY OF NATAL

EXAMINATIONS : NOVEMBER 1995

SUBJECT, COURSE AND CODE : CHEMISTRY 224 : PHYSICAL : PCHM2PP2

DURATION: 2 HOURS **TOTAL MARKS: 100**

External Examiner: Professor M Sankar
University of Durban-Westville

Internal Examiner: Professor W A Hawksworth

Notes: This Paper consists of **6** pages
Please see that you have them all.

The use of non-programmable electronic calculators is permitted.

STUDENTS ARE REQUESTED, IN THEIR OWN INTERESTS, TO WRITE LEGIBLY

ANSWER FOUR QUESTIONS, AT LEAST ONE QUESTION MUST BE FROM SECTION B

SECTION A

QUESTION 1

a) Use the Frank and Wen model to distinguish between a structure making ion and structure breaking ion.

(4)

b) Compare the mechanism of migration of the cation and anion in a dilute HCl solution during electrolysis.

(5)

c) Given the following molar conductances at infinite dilution:

CsCl : 154,6 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$
CsOH : 271,0 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$

If the molar conductance of the Cs^+ ion at infinite dilution is 77,26 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ calculate the transport number at infinite dilution of the Cs^+ ion in CsCl and CsOH solutions.

(5)

d) The resistance of a conductivity cell dipping into a solution of 0,1 M KCl was 78 ohm and when the same cell was placed in 0,1 M 2:2dimethylpropionic acid the resistance measured 2510 ohms.

Calculate: i) The cell constant
ii) The molar conductance of 0,1 M 2:2dimethylpropionic acid solution.
iii) The dissociation constant of 2:2 dimethylpropionic acid.

The conductivity of 0,1 M KCl = 0,01287 ohm^{-1} cm^{1}. The molar conductance at infinite dilution of 2:2 dimethylpropionic acid is 417 ohm^{-1} cm^{2} mol^{-1}

(11)

[25]

QUESTION 2

a) Briefly describe 3 electrodes that can be used to measure the pH of a solution.

(5)

b) For the following electrochemical cell:

$$\overset{-}{Zn} \,|\, ZnSO_4(aq) \,|\, Hg_2SO_4(s), \overset{+}{Hg}$$

Deduce:

i) The spontaneous cell reaction
ii) An expression for the cell e.m.f. in terms of the standard electrode potentials and the concentration of the $ZnSO_4$ solution.
iii) The concentration of $ZnSO_4$ required in the cell to give an overall cell e.m.f. of 1,5000 volts at 25°C.

$$E^\circ_{Zn/Zn^{2+}} = -0{,}7628\ V \quad E^\circ_{Hg,Hg_2SO_4/SO_4^{=}} = +\ 0{,}6151\ V$$

R the gas constant = 8,314 J K^{-1} mol^{-1}
F the faraday = 96500 C mol^{-1}

(8)

c) Measurements on an electrochemical cell in which the following 2 electron transfer reaction takes place:

$$Pb(s) + Hg_2SO_4(s) = 2Hg(l) + PbSO_4(s)$$

gave the following results:
The standard cell e.m.f. at 25°C = 0,9710 V.
The temperature coefficient of the standard cell e.m.f. = $-3,8 \times 10^{-4}$ V K^{-1}.

i) Use the standard notation, to represent this cell.
ii) Calculate the standard free energy change $\Delta G°$, the standard enthalpy change $\Delta H°$ and the standard entropy change $\Delta S°$ for the cell reaction at 25°C.
iii) Calculate the equilibrium constant for the cell reaction at 25°C.

F, the faraday = 96500 C mol^{-1}.

(12)
[25]

QUESTION 3

a) 1L of perfect monatomic gas is initially at 273,2 K and 10 atm. If this gas is allowed to expand isothermally and reversibly to a final pressure of 1 atm, calculate the work done, heat transferred and the change in internal energy.
R, the gas constant = 8,31442 J K^{-1} mol^{-1}.
1 atm = $1,01325 \times 10^5$ Pa.

(8)

b) The gas of question a) expands adiabatically and reversibly from an initial pressure of 10 atm and temperature of 273,2 K. Determine the final temperature and volume of the gas. (The molar heat capacity is $C_v = \frac{3}{2}R$; you will need to work out the ratio $\gamma = C_p/C_v$.)

(5)

c) The enthalpy of combustion of ethane at 298 K is -1510,6 J mol^{-1}. Calculate the temperature rise in 1 kg of water that would result from combustion of 0,1816 mol ethane. Assume that the heat capacity of water is 4,184 J K^{-1} g^{-1}.

(4)

d) The enthalpy of vaporization of cyclohexane at its normal boiling point of 80,7°C is 33,0 k J mol^{-1}. Assuming that the heat capacities of the liquid and vapour are 156 J K^{-1} mol^{-1} and 106 J K^{-1} mol^{-1} respectively, estimate the enthalpy of vaporization of cyclohexane at 25°C.

(4)

e) Determine the standard enthalpy of the reaction:

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.5H_2O(s)$$

From the following standard enthalpies of formation:

$CuSO_4(s)$	ΔH°_f = -771,4 kJ mol^{-1}
$H_2O(l)$	-285,8 kJ mol^{-1}
$CuSO_4.5H_2O(s)$	-2279,7 kJ mol^{-1}

(4)

[25]

QUESTION 4

a) The enthalpy of vaporisation of n-heptane is 37,0 kJ mol^{-1} at its normal boiling point of 98,4°C. Calculate the entropy change experienced by 1 mol of heptane when it vaporizes reversibly at this temperature.

(3)

b) 3,567 mol of perfect gas at 300 K expands reversibly and isothermally until its volume has trebled. Calculate the entropy change experienced by the gas. Would your result be different at another temperature? Explain.

(6)

c) The molar heat capacity C_p of As is 24,64 J K^{-1} mol^{-1} at 298 K. Assuming this heat capacity to be temperature - independent, determine the entropy change experienced by 100 g As when its temperature is increased from 298 K to 348 K. (The molar mass of As is 74,92 g mol^{-1}.)

(4)

d) A 100 g block of ice initially at 0°C is allowed to melt by putting it in contact with its surroundings at 25°C. Given that the enthalpy of fusion of ice is 6,008 kJ mol^{-1} and the molar heat capacity of water is 75,38 J K^{-1} mol^{-1}, calculate the entropy changes experienced by the ice (the system), the environment and the universe. (Molar mass of water is 18.02 g mol^{-1}.)

(12)

[25]

SECTION B

QUESTION 5

a) Consider a reaction

$$A + B \rightarrow C$$

which is first order with respect to both A and B. Integrate the rate equation for this reaction and derive an expression for the rate constant of the reaction in terms of the initial concentrations of the reactants. The initial concentrations of the reactants **may not** be assumed to be equal.

(12)

b) A solution of A is mixed with an equal volume of a solution of B containing the same number of moles, and the following reaction occurs

$$A + B \rightarrow C$$

At the end of 1 hour A is 75 percent reacted. How much of A will be left unreacted at the end of 2 hours if the reaction is first order with respect to both A and B.

(8)

c) Give an account of the half-life method for the determination of the order of a reaction.

(5)

[25]

QUESTION 6.

a) Explain what is meant by the terms:-

- i) Moleculartiy of a chemical reaction.
- ii) Rate constant of a chemical reaction. What would be the appropriate units in which to express the rate constant of a second-order reaction?
- iii) Pseudo first order reaction.

(7)

b) The reaction:

$$\delta A + \beta B + \gamma C \rightarrow \text{Products}$$

has a rate equation:

$$\text{Rate} = k[A]^{n1}[B]^{n2}[C]^{n3}$$

Explain how you would determine the overall order of this reaction using the graphical method

(6)

c) The decomposition of compound A is a first order reaction with an activation energy of 52,3 kJ mol^{-1}. At 283 K the rate constant is 2,0 x 10^{-4} S^{-1}. Calculate the percentage decomposition of A that would be observed after 20 minutes at 293 K.

(6)

d) Show that $t_{½} \; \alpha \; \frac{1}{[A]^{n-1}}$ for a reaction that is nth order in A.

(6)

[25]

Question 1.

(a) ~~In some textbooks the First Law of Thermodynamics is stated as~~

$$\Delta U = q - w$$

~~where q refers to heat, w to work and ΔU to the internal energy change. Is the work in this statement performed on or by the system?~~ (1)

(b) ~~State the First Law for a system which absorbs heat q_p for a~~ [illegible] ~~at constant pressure p and in doing so changes its volume by ΔV.~~ (1)

(c) 1 L of perfect monatomic gas with $\gamma = \frac{5}{3}$ is initially at 273.2 K and 10 atm. If this gas is allowed to expand ~~adiabat~~ isothermally and reversibly to a final pressure of 1 atm, calculate the work done, heat transferred and the change in internal energy. (8)

(d) Repeat the calculation of part (c), assuming that the expansion takes place adiabatically and reversibly from an initial pressure of 10 atm and temperature of 273.2 K. Determine the final temperature ~~of~~ and ~~the~~ volume of the gas, and the internal energy change ($C_V = \frac{3}{2}R$) (5)

(e) Given the following thermochemical data

$C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H_{298} = -1560.1$ kJ

$C(gr) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_{298} = -393.5$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H_{298} = -285.8$ kJ

Calculate the enthalpy of formation of ethane

~~C_2H_6~~ $2C(gr) + 3H_2(g) \rightarrow C_2H_6(g)$

at 298 K. (5)

(f) From the enthalpy of combustion of ethane given above, calculate the rise in the temperature of 1 kg water that would be produced by combustion of 0.1816 mol of ethane. (Assume that the heat capacity of water is 4.184 $J K^{-1} g^{-1}$). (5)

(g) The enthalpy of vaporization of cyclohexane at its boiling point of 80.7 °C is 33.0 $kJ\,mol^{-1}$ ~~and the~~ Assuming that the heat capacities of the liquid and vapour are 156 $J K^{-1} mol^{-1}$ and 106 $J K^{-1} mol^{-1}$ respectively, ~~calculate~~ estimate the molar enthalpy of vaporization of cyclohexane at 25 °C. (5)

(h) Determine the standard enthalpy of the reaction

$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 \cdot 5H_2O(s)$ (3)

from the ~~[illegible]~~ standard enthalpies of formation:

$CuSO_4(s)$: −771.4 $kJ\,mol^{-1}$; $H_2O(l)$: −285.8 $kJ\,mol^{-1}$; $CuSO_4 \cdot 5H_2O(s)$: −2279.7

Model Answer

1. (a) In $\Delta U = q - w$, w is the work done by the system. 1

(b) The work done on the system is $-p\Delta V$. The first law says that

$$\Delta U = q_p - p\Delta V \quad 1$$
$$= \Delta H - p\Delta V$$

(c) $T_1 = 273.2$, $P_1 = 10 \text{ atm} = 1.013 \times 10^6 \text{ Pa}$, $V_1 = 1 \text{ L}$

$$n = \frac{P_1 V_1}{RT_1} = \frac{(1.013 \times 10^6 \text{ Pa}) \times (1 \times 10^{-3} \text{ m}^3)}{(8.314 \text{ JK}^{-1}\text{mol}^{-1}) \times (273.2 \text{ K})}$$

$$= 0.4460 \text{ mol} \quad 1$$

$$V_2 = 10 \text{ L} \quad \text{since } P_1V_1 = P_2V_2 \quad 1$$

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right) \quad 1$$

$$= -(0.4460 \text{ mol}) \times (8.314 \text{ JK}^{-1}\text{mol}^{-1}) \times (273.2 \text{ K}) \times \ln 10$$

$$= -2.333 \text{ kJ} \quad 1$$

$\Delta U = 0$ 1 $\therefore$ $q = -w$ 1

$$= 2.333 \text{ kJ}$$

The heat capacity ratio is $\gamma = C_p/C_v = (1 + \frac{3}{2})/\frac{3}{2} = \frac{5}{3}$ 1

(d) For adiabatic reversible process

$$pV^\gamma = \text{constant}$$

$$P_1V_1^\gamma = P_2V_2^\gamma \quad 1$$

$$\left(\frac{V_2}{V_1}\right)^\gamma = \frac{P_1}{P_2} = \frac{10}{1} \quad 1$$

$$\frac{V_2}{V_1} = 10^{3/5} \quad 1$$

$$V_2 = 1 \text{ L} \times 10^{3/5}$$

$$= 3.981 \text{ L}$$

$$T_2 = \frac{P_2V_2}{nR} = \frac{(1.013 \times 10^5 \text{ Pa}) \times (3.981 \times 10^{-3} \text{ m}^3)}{(0.4460 \text{ mol}) \times (8.314 \text{ JK}^{-1}\text{mol}^{-1})} = 108.8 \text{ K} \quad 1$$

(f) Enthalpy of combustion

= −1560.1 kJ mol^{-1}

Heat produced by combustion of 1.816 mol

q = (1.816 mol) × (−1560.1 kJ mol^{-1})

= −283.31 kJ 1

Temperature rise:

$q = mc\Delta T$ 1

1 $\Delta T = \frac{q}{mc}$

$= \frac{+283.31 \text{ kJ}}{(4.184 \text{ J K}^{-1}\text{g}^{-1}) \times (1000 \text{ g})}$

= 67.7 K 1

(g)

$$\begin{tikzcd}
C_6H_{12}(l, 80.7°) \arrow[r, "33.0 kJ mol^{-1}", "\Delta H_2"'] & C_6H_{12}(g, 80.7°C) \arrow[d, "\Delta H_3"] \\
C_6H_{12}(l, 25°C) \arrow[u, "\Delta H_1"] \arrow[r, "\Delta H"'] & C_6H_{12}(g, 25°C)
\end{tikzcd}$$

1

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

1 ΔH_1 = (1 mol) × (156 J K^{-1} mol^{-1}) × (55.7 K)

= 8.7 kJ

ΔH_2 = 33.0 kJ

1 ΔH_3 = (1 mol) × (106 J K^{-1} mol^{-1}) × (−55.7 K)

= −5.9 kJ

∴ 1 ΔH = 8.7 + 33.0 − 5.9 = 35.8 kJ mol^{-1}

(h) Enthalpy of reaction

$$\Delta H = \sum \nu_i \Delta_f H_{i,0}$$

$$= 1 \times \Delta_f H^\circ [CuSO_4 \cdot 5H_2O(s)]$$

$$- 5 \times \Delta_f H^\circ [H_2O(l)]$$

$$- 1 \times \Delta_f H^\circ [CuSO_4(s)]$$

$$= 1 \times (-2279.7) + (-5) \times (-285.8) + (-1) \times (-771.4)$$

$$= 771.4 + 1429 - 2279.7$$

$$= -79.3 \text{ kJ mol}^{-1}$$

Question 2

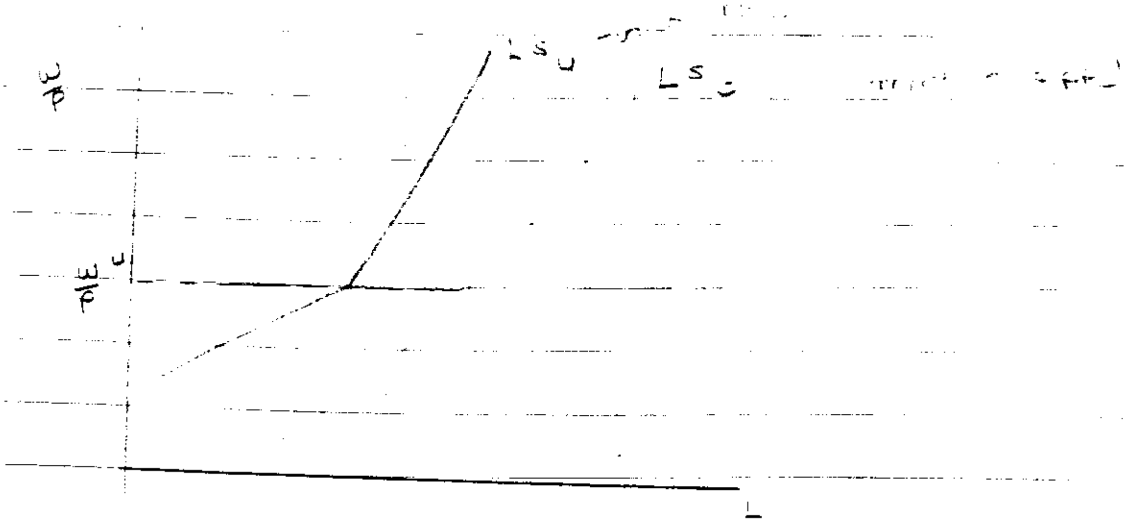
(a) The enthalpy of vaporization of n-~~pentane~~ heptane is 37 kJ mol^{-1} at its normal boiling point of 98.4°C. Calculate the entropy change experienced by 1 mol of heptane when it vaporizes reversibly at this temperature. (3)

(b) 3.567 mol of perfect gas at 300K expands reversibly and isothermally ~~at 300K~~ until its volume has trebled. Calculate the entropy change experienced by the gas. Would your value be different at another temperature? Explain. (6)

(c) ~~Calculate the Entropy~~ The molar heat capacity C_p of As is 24.64 J K^{-1} mol^{-1} ~~Calculate the entro~~ at 298 K. Assuming this heat capacity to be temperature-independent, determine the entropy change experienced by 100 g As when its temperature is increased to 348 K. (molar mass of As is 74.92 g mol^{-1}). (4)

(d) A 100 g block of ice initially at 273 K is allowed to melt by putting it in contact with surroundings at 298 K. Given that the enthalpy of fusion of ice is 6.008 kJ mol^{-1} and assuming that the heat capacity of water is 4.184 J K^{-1} g^{-1} calculate the entropy changes experienced by the ice, the surroundings, and the universe.

diag [illegible]



T. union - less elastic above going wage
- more elastic below going wage

5.33 Trade unions and labour demand

i) labour market demand acts as a [illegible] on Trade union action

- Trade union [illegible] with the [illegible] demand for labour
- remember the conditions of Marshall Hicks which correlate with inelastic LD:
  - inelasticity of product D
  - capital intensity
  - low elasticity of substitution of L with K or L with Ln
- inelasticity supply of substitutable factors

- expect T unions in capital intensive large scale (imperfect [illegible] firms

Model Answer

2(a) Entropy change is

$$\Delta S = \frac{\Delta H_{vap}}{T_b} \quad 1$$

$$= \frac{(37.0\,kJ\,mol^{-1})}{(371.55\,K)} \quad 1$$

$$= 99.6\ J\,K^{-1}\,mol^{-1} \quad 1$$

(b) $n = 3.567$ mol

$$q_{rev} = nRT\ln\left(\frac{V_2}{V_1}\right) \quad 1$$

$$V_2 = 3V_1 \quad 1$$

$$\therefore \Delta S = \frac{q_{rev}}{T} = nR\ln\left(\frac{V_2}{V_1}\right) \quad 1$$

$$= (3.567\,mol) \times (8.314\,J\,K^{-1}\,mol^{-1}) \times \ln(3)$$

$$= 32.58\ J\,K^{-1} \quad 1$$

Would not be different, since q is proportional to T when ΔS is calculated T cancels. 2

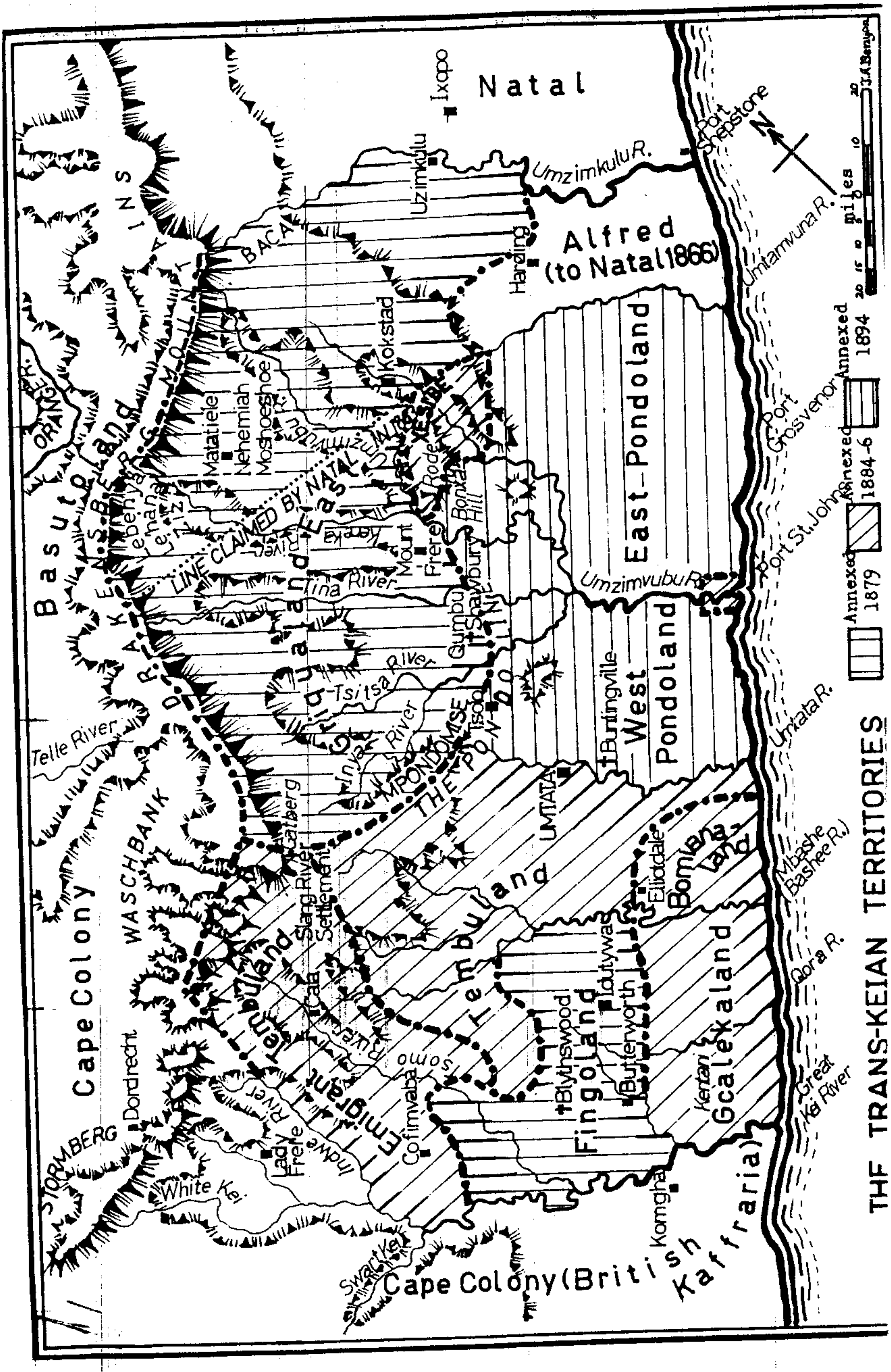
(c) Molar mass $= 74.92\ g\,mol^{-1}$ $\qquad C_p = 24.64\ J\,K^{-1}\,mol^{-1}$

$$\therefore n = \frac{(100\,g)}{(74.92\,g\,mol^{-1})} = 1.335\ mol \quad 1$$

$$\Delta S = nC_p\ln\left(\frac{T_2}{T_1}\right) \quad 1$$

$$= (1.335\,mol) \times (24.64\,J\,K^{-1}\,mol^{-1}) \times \ln\left(\frac{348}{298}\right)$$

$$= 5.102\ J\,K^{-1} \quad 1$$



THE TRANS-KEIAN TERRITORIES

(b) No. of moles $= \frac{100\,g}{18.02\,g\,mol^{-1}}$

$= 5.549\ mol$

Heat absorbed by melting: $q = n\Delta H_{fus} + mc_s \Delta T$

$q = (5.549\ mol) \times (6.008\ kJ\,mol^{-1})$

~~$+ (5.549\ mol) \times$~~ $+ (100\,g) \times (4.184\ J\,g^{-1}K^{-1}) \times (25\,K)$

$= 33.34\ kJ + 10.46\ kJ$

$= 43.80\ kJ$

Entropy change for ice: $\Delta S_{sys} = \frac{n\Delta H_{fus}}{T_m} + mc \ln\left(\frac{T}{T_m}\right)$

$\Delta S_{sys} = \frac{(33.34\ kJ)}{(273.2\,K)} + (100\,g) \times (4.184\ J\,K^{-1}g^{-1}) \times \ln\left(\frac{298.2}{273.2}\right)$

$= 122.04 + 36.64$

$= 158.7\ J\,K^{-1}$

Entropy change for surroundings

$\Delta S_{env} = -\frac{q}{T}$

$= -\frac{(43.80\ kJ)}{298.2\,K}$

$= -146.9\ J\,K^{-1}$

Total entropy change

$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{env}$

$= 158.7 - 146.9$

$= 11.8\ J\,K^{-1}$

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27 September 1995

Dear Simon

re: Impressions of Chem 2 lecture (Chemical Thermodynamics), 1.15, 21 September 1995

You asked me to sit in on the fourth of a series of lectures on Chemical Thermodynamics at second-year level, to give you my impressions on the following;

- were the main points coming across?
- was there a logical structure to the lecture and was this apparent?
- were you "doing anything to inhibit the transmission of what [you were] trying to convey?"

At the outset I would like to reiterate what we discussed beforehand, that is that it's very difficult to evaluate somebody's teaching on the basis of one site-visit, and that to get a more holistic picture it would be necessary to run at least a student evaluation as well. We can perhaps do that following this initial meeting. Nevertheless, there is a fair amount that can be gauged about clarity, atmosphere in the class, student participation and so on.

The 45 - 50 students present at the lecture settled very quickly, and appeared to know what to expect. I noted that the seating patterns were similar to that in most courses, i.e. even spread, predominantly black students in the front, white students at the back (except that in this class about 65% of the students were African). As they were settling I asked those around me (in the back two rows) how they found the course - the responses were "it's fine", and "enjoyable".

In your introduction you said you were "continuing a conversation" and would be explaining adiabatic processes, and summarised the main conclusions of the last lectures i.e. the formulae arrived at. This seemed to be appreciated by the students, they knew where they were and what was coming - I noticed them going over the handouts which you had distributed as they came in. Given the word "conversation", however, I expected that there would be more two-way conversation - but more of that later.

The students were attentive all the way through and content to take notes. I saw that those around me were able to take clear notes, and had the time to write formulae and other important items in a different coloured pen, as you did when noting what the assumptions were in different processes on the chalkboard. Your pace was suited to the students' thus, and it was helpful that you wrote down everything you expected them to get down on the board. Your writing on the board was perhaps a bit small and faint, but the yellow chalk was nevertheless legible from the back. I thought you spoke clearly and audibly, and changed tone when you explained something. I thought more explanations might have been necessary - it was difficult for me to tell how much the students were understanding and how familiar they were with the concepts involved - I noticed one girl looking slightly puzzled at one point, but then was satisfied after a brief question to her neighbour. The questions from students at the end indicated that they at least had been following all the steps. In answer to the first question then, "were the main points coming across", I can say that, as a non-chemist, it was abundantly clear what the main points were; whether students had internalised them I can't really say. I would like to be able to ask them that.

The structure of your lecture was very clear, first laying out the theoretical principles in the first half of the lecture - the "serious" bit, whereafter you explained to students what you expected them to know and to be able to do. At this point there was a slight buzz in the room, a visible relaxation after "getting the important bits down". You then went through the examples, wrote up the whole problem and gave the solutions. Five minutes before the end you summarised the main points of this lecture, and provided the students with a verbal "checklist" of the learning objectives of this lecture, and said what they didn't need to know, which is also important in building confidence. Similarly, I thought your handouts were very clear and well put together, detailed and thorough, and I think it's good that you give students an idea of why certain things are important and how they relate to real issues. The learning objectives too, are well defined and the rationale behind the choice of problems is explicit. The answer to your second question, about the logical structure being apparent, is thus an affirmative.

I did wonder though if it wouldn't be possible to involve students more in the examples part of the lecture - would they not be able to identify the assumptions for instance? I don't think the class is too big for active participation, and the atmosphere was quite comfortable - I think the students might respond well to that sort of stimulus. After all, they have got the main things down, and they are provided with a handout that summarises the material, the problems and the expectations neatly. So they have security and back-up with respect to the material - the absence of which usually undermines the success of more informal, participatory lectures.

This leads me to your third question; "were you doing anything to hinder transmission?". The answer to this is no. The operative word here, however, is 'transmission'. As I said to you afterwards, I thought the lecture was very clear, the material and explanations very solid, but perhaps a bit dry. (I did think though, that this may have been related to my presence in the class). This could be alleviated through encouraging greater student participation - students constructing their knowledge (you mentioned to me that you thought favourably of "constructivism" as it applies to teaching), rather than simply receiving a transmission. On the other hand, the students are provided with problems through which they can apply their theoretical understanding, and I understand that the practicals are designed to complement the lectures and give students a chance to do some of that "constructing" of knowledge.

All in all then, in the three areas you asked me to look at, my impressions of the lecture are positive ones. In order to answer the first question more fully though, and to ascertain the students' perspectives on their learning experience, I recommend that we run a student evaluation along the lines of those used in other courses towards the end of the section.

Yours sincerely

Denyse

Denyse Webbstock
Evaluator
CUED

CHEMISTRY 224, 1995

COURSE EVALUATION QUESTIONNAIRE REPORT

November 1995

A course evaluation questionnaire drawn up by the CUED evaluator, and adapted for use in Chem 224 by the course lecturer was administered to the Chem 224 cohort during a lecture period in the last week of lectures of the second semester of 1995. A total of 46 students completed the questionnaire out of a possible .. registered for the course. Few of the respondents provided further comment to the 25 questions in the computerised section of the questionnaire.

In the questionnaire, students were presented with positively phrased statements (with one or two exceptions), to which they could respond on a five-point scale; they could either **A. strongly disagree, B. disagree, C. be neutral, D. agree, or E. strongly agree.** For the purposes of analysis, and to gauge a mean response, each category was awarded a numerical value, i.e. 1 for strongly disagree, 5 for strongly agree. Categories A & B were considered to be negative responses, D & E positive ones.

All student comments included in the report are quoted verbatim.

General

58% of the respondents reacted positively to the question on whether Chemistry 224 had met their expectations; 4% disagreed, mean 3.8. A little more than half (54%) had understood from the course outlines what was expected of them; 17% had not. 84% thought that this course was well-organised; 9% disagreed.

63% found that it had been made clear how different concepts developed fitted together, while 20% disagreed, mean 3.7. 52% found they could use things they learnt in Chem 224 in their other courses; 22% found otherwise.

48% of the respondents was enthusiastic about studying Thermodynamics, 20% was not. 60% found that they had been given sufficient guidance to help them cope with their studies; 22% disagreed. 44% found that this course encouraged them to work independently; 24% disagreed. 57% had learnt to think in new ways as a result of studying Thermodynamics; 13% had not. 72% felt that they had developed intellectually beyond the point they were at when they started the course; 13% disagreed. 35% found the workload for this course to be greater than for their other courses; for 46% this was not the case.

Two-thirds of the respondents would recommend this course to other students; 15% would not, mean 3.8.

The only comment received on the General section was "tutorial work should be considered more seriously by students". Why there were not more comments is not clear; perhaps students did not have sufficient time to comment.

From the above data it is clear that the majority of students considered this to be a well organised course, which helped them to develop in the field. It is also clear, however, that levels of enthusiasm for the subject are relatively low. This does not appear to be related to an excessive workload, which is sometimes a reason for reducing enthusiasm.

Lectures. Prof. Marshall's

78% of the respondents found Prof. Marshall's lectures to be clear and well delivered; 56% agreeing strongly that this was so. 13% disagreed. The mean response to this question was 4.1. 78% found that the level at which these lectures were pitched was just right for them; 16% disagreed, mean 3.9. 74% said they could always understand the language used in these lectures; 16% said they could not. There were fairly similar responses to the question concerning clear explanation of concepts, i.e. 67% positive; 16% negative. On the question whether students could take adequate notes in these lectures the response was 84% positive, 9% negative.

36% understood how to discriminate between important and less important information in these lectures; 9% felt they could not, and 56% was neutral. 58% thought they would be able to transfer concepts they had learnt in these lectures to other topics; 16% disagreed.

64% of the respondents found these lectures challenging; 20% did not. 80% considered this section to be carefully prepared; 11% thought otherwise. 71% thought that good use had been made of course materials such as handouts; 11% disagreed. 63% of the respondents considered Prof. Marshall to have a good relationship with the class; 13% thought otherwise, mean 3.8. 58% found that Prof. Marshall inspires enthusiasm for studying Thermodynamics; 16% disagreed, mean 3.6. 75% were confident that Prof. Marshall would have been willing to help them solve difficulties had they gone to see him; 12% were not.

From the above responses the impression emerges of a lecturer considered to be thorough and competent by most of his students, who explains well and is generally willing to help students with difficulties. Lectures appear to be pitched at a level these students find appropriate. There is perhaps room for improvement in finding ways of "cuing" students on the levels of importance of different bits of information, and in finding ways of inspiring their enthusiasm for the subject to a greater extent.

The few comments received bear this impression out; they are here quoted in full.

"Excellent teacher. I propose that all lecturers give us time for comments. I feel it's really helpful to comment this way", "the teaching style he uses is excellent and well organised. The pace is normal and acceptable. He make the course easier by explaining concepts explicitly", "I did go to see him and he was willing", "thank God it's over!! (Hopefully..)", "on a few occasions the discernment between important points and the lesser important material was difficult", "very well lectured", and "good lecturer. Keep it up".

Denyse Webbstock
CUED

Chemistry 224 - Thermodynamics

Course Evaluation Questionnaire

In this questionnaire you will be asked your opinion on various aspects of the Thermodynamics component of Second Year Physical Chemistry, for the the purposes of evaluation. In each question you are presented with a statement to which you should respond on the computerised answer sheet. Your possible answers are:

A Strongly disagree
B Disagree
C Neutral response
D Agree
E Strongly Agree

Fill in your answer on the right hand side of the answer sheet under answers 1- 25. Please use an HB pencil only. Please note that the questionnaire is anonymous. You do not need to complete the sections on the answer sheet concerning student number, name, sex, grade, date or special codes. In the block marked 'additional data' write Chemical Thermodynamics under 'course' and your matric. educational authority, e.g. HoD, DET, NED etc. under 'name'. You are requested to complete the questionnaire in this period, and hand it in at the end. Any additional comments you have may be written in the spaces provided on the question sheet. Thank you for your cooperation.

The purpose of this evaluation is to help Prof. Marshall to see what needs to be changed and what doesn't. Please be constructive! If you feel something does not work as well as it could, pleased suggest how it could be improved.

General

1. I feel that the Thermodynamics part of Chemistry 224 has met my expectations of it.
2. I understand from the course outlines what was expected of me in this part of the course.
3. I thought this course was well organised.
4. It was made clear to me how the various concepts developed fitted together.
5. I found that I could use things that I learned in this course in my other courses.
6. I feel enthusiastic about studying Thermodynamics.
7. I feel in general that I have been given sufficient guidance in order to help me cope with my studies in Chemistry.
8. This course encouraged me to work independently.
9. As a result of studying Chemistry I have learnt to think in new ways.
10. At the end of this course, I feel that I have developed intellectually beyond the point I was at when I started the course.
11. I found the workload for this course greater than for my other courses.
12. I would recommend this course to other students.

Honours Physical Chemistry: Statistical Thermodynamics

Scope and Significance

Undergraduate Physical Chemistry courses can be regarded as consisting of two main themes. On the one hand, increasingly sophisticated models for the properties of individual molecules are developed - for example, with the introduction to spectroscopy and quantum mechanics, and the use of molecular orbital concepts to explain reaction mechanisms and trends in the stability of compounds. On the other hand, the principles of thermodynamics are developed from a largely macroscopic perspective that emphasises the relation of the thermodynamic functions to measurable energy changes and physical properties of pure substances and mixtures. Only in the case of the entropy function is an attempt made to provide an interpretation in terms of the molecular configurations accessible to a substance.

The significance of Statistical Thermodynamics is that it allows a connexion to be established between these two divergent views of matter. In particular, it demonstrates that the intuitively-appealing qualitative view of entropy as a measure of configurational disorder in an assembly of molecules can be made rigorous and quantitative.

Background of Students

The students in this course are assumed to have completed the requirements for a BSc degree with specialisation in chemistry, for which a prerequisite is at least one First-Year course in mathematics. As a result of the Second-Year course, they should be familiar with the three Laws of Thermodynamics, and from the Third-Year course, they should be familiar with basic concepts of spectroscopy as applied to diatomic molecules, and elementary concepts of quantum mechanics. In the Honours Core course in Physical Chemistry, which is taught in the first half of the year, their knowledge of spectroscopy is extended by introduction to the group-theoretical analysis of molecular symmetry and vibrations. The thermodynamic characterisation of nonideal systems is also considered, with particular reference to the Principle of Corresponding States and its use in the calculation of virial coefficients and fugacity coefficients in gases and gas mixtures.

General Characteristics of Teaching Strategy

From an early stage in our education as chemists, molecular models have been invoked to explain the behaviour of matter. While on the one hand it is intuitively attractive to be able to predict the thermodynamic functions and the properties of substances from molecular considerations, on the other hand the mathematical apparatus required for this purpose makes Statistical Thermodynamics virtually inaccessible to most students. It is particularly important for the students to be able to separate the physical implications of the various models from the analytical manipulations involved in the construction of these models. Published expositions of Statistical Thermodynamics do not succeed in making this separation. Those intended for use by physical chemists generally include Statistical Thermodynamics as a (usually small) part of a course in General Physical Chemistry covering an extremely wide range of topics, and as a result, insufficient attention is paid to fundamental concepts. Treatments intended for physics students are more rigorous and focussed, but generally assume a quite strong mathematical background on the part of the students. Consequently, neither type of treatment can be expected to be suitable for mathematically weak students.

The teaching strategy that I have developed with these limitations in mind is based upon the identification of the distribution function (*i.e.*, the probability density function) as the unifying central concept in the development of a statistical treatment of molecules. At the same time as the fundamental physical concepts are introduced, students work through examples that illustrate the important properties of various types of distribution functions, *viz.*, normalisation, computation of expectation values and cumulative probability distributions. The examples selected for this purpose include the functions that arise later in the exposition of the statistical-mechanical theories. The idea of this is that in these later stages of the course, emphasis can be devoted to the physical implications of the models, since the formal operations involved have already been carried out as a purely mathematical exercise.

The logical-expository approach adopted by Physical Chemistry textbooks and monographs on Statistical Thermodynamics is not only highly dependent on analytical manipulations, but also on the particular argument used to develop the subject. This is evidently a rather inefficient way of learning, because a reasonably profound grasp of the subject would have to be synthesised by reading many different expositions. A more promising approach would encourage students to construct their knowledge by comparing their views of what would constitute physically reasonable behaviour with what is predicted by the various models and, of course, with what is observed experimentally. Although this constructivist approach is widely used in the development of elementary-level science curricula (such as the Science Foundation Program in this University), it seems particularly appropriate for a course in Statistical Thermodynamics, in view of its inherent compatibility with the hypothetico-deductive character of the subject. The constructivist approach is implemented in practice by commencing a lecture with questions designed to focus attention on the essential physics and to identify the parameters required to specify the state of the system under consideration, proceeding to the analysis, and finally returning to the comparison of the basic physical behaviour with the predictions of the models.

A further important element of the teaching strategy is the analysis of the subject matter into specific learning objectives corresponding to a range of cognitive skills. I feel that such an analysis is particularly important for Statistical Thermodynamics, since it is often unclear to students (as it was to me as an undergraduate) whether they should be able to derive the formulae, apply them to generate new theoretical results, or merely use them to provide numerical estimates of various physical quantities. Excessive concentration on the formal analytical aspects can (and often does) lead to deficiencies in understanding that become apparent when students are forced to confront various types of problems. It is much better to encourage students to be able to identify relevant assumptions and approximations, and to describe the physical arguments behind the various results, than to expect them to reproduce derivations from memory.

Synopsis of Content and Teaching Strategies

Lecture No. 1

In the first part of this lecture, an intuitive justification for a statistical description of matter is presented. The idea of characterising a system in terms of microstates is used to introduce the postulate of equal *a priori* probabilities, and the concept of an ensemble of systems large enough to represent all possible configurations is used to introduce the ergodic hypothesis. Attention is then turned to the basic statistical concepts that find application in Statistical Thermodynamics, in particular the probability density function, normalisation, expectation values and statistical independence. Finally, the exponential form of the Boltzmann distribution is derived by application of the concept of statistical independence to the energy in a system of weakly-interacting particles, and the significance of the partition function as the normalising constant for this distribution is demonstrated. This simple, intuitively-appealing derivation is based closely on the exposition presented by Jackson (1968).

Lecture No. 2

Here, the more usual derivation of the Boltzmann distribution from the combinatorial problem of distributing members of a canonical ensemble among accessible energy states is presented. The basic goal here is to demonstrate that the Boltzmann distribution is the most probable distribution that is consistent with the constraints that the total energy and number of members of the ensemble are constant. This is the development generally presented in Physical Chemistry texts and monographs on Statistical Thermodynamics (*e.g.*, Reif, 1966; Moore, 1972, Atkins, 1990). The different approaches presented in this and the previous lecture are used to demonstrate different aspects of the physical significance of the various quantities.

Lecture No. 3

In this lecture, the connexion between the thermodynamic functions and the partition function is developed. The first important points here are that the internal energy can be identified with the expectation value of the Boltzmann distribution for the energy, and that this is the same result as that obtained by logarithmic differentiation of Z with respect to β. With this established, the log of the partition function for the system is assumed to be a function of T and V, and the differential of $\ln Z$ is compared with the differential form of the Combined First and Second Laws. This leads to the result that β is inversely proportional to T, and the identification of pressure and entropy in terms of Z. Finally, the concept of the statistical uncertainty is introduced, and used to establish an alternative formula for the entropy in terms of the probabilities of accessible configurations of the system. The development here again is based on that presented by Jackson (1968).

Lecture No. 4

This lecture is designed to reinforce and make definite the concepts presented so far. It takes the form of a class exercise, in which the partition function and the thermodynamic functions are worked out for an hypothetical system of particles that can assume five equally-spaced energy levels that are integer multiples of a dimensionless energy parameter $\beta\varepsilon$. The exercise is introduced with the focus question, 'How do you think the distribution of particles among these accessible states will be affected by the value of $\beta\varepsilon$?' It is designed to lead the students to the conclusion that the preference of the particles for one energy level over another is crucially dependent on this quantity (which measures the separation between adjacent energy levels), that the entropy obtained in the manner described can be intuitively related to the degree of information we have about the state of the system, and that the size of the partition function is a measure of the accessible volume of phase space. The establishment of an intuitive, as distinct from a purely formal appreciation of these facts can be identified as the central goal of the course, and is a theme recurring through the subsequent analyses of particular molecular systems.

Lecture No. 5

In this lecture, the apparatus of statistical mechanics developed in the previous classes is applied to the simplest possible physical system: the classical monatomic perfect gas in the absence of external fields. Attention is focussed on the essential physical characteristics of this system by posing the questions, 'Do you think that a given atom of the gas is more likely to be found in one part of the container than another?', 'Do you think that a given atom is more likely to be travelling in one direction than another?', and 'How can we describe a given microstate of the gas and determine its energy?'. The answer to this last question is dependent on the answers to the first two, and leads naturally to to the expression of the partition function in terms of the velocity components of the N atoms. At this point the concept that the partition function needs to be made dimensionless by division by a scale factor is introduced, with the observation that its actual value is immaterial since it contributes at most an arbitrary additive constant to the thermodynamic properties (which are all expressed in terms of $\ln Z$). The partition function for the gas is expressed in terms of the atomic partition function by making the further observations that the integrations over the velocity coordinates are equivalent, and that in view of the indistinguishability of the atoms, the partition function needs to be divided by $N!$ (The argument followed by Reif (1966) initially assumes that the particles are distinguishable, and uses the Gibbs paradox to justify, in an *ad hoc* manner, the incorporation of this factorial, while Jackson (1968) shows that it results from considering the general treatment of degenerate quantum gases. These two approaches are felt to be rather circuitous for an introductory course.) Finally, application of the results derived earlier leads to the deduction of the perfect gas equation of state, the identification of Boltzmann's constant in terms of the gas constant, and the expression for the molar internal energy as $3RT/2$.

Lecture No. 6

The purpose of this lecture is to deduce the Maxwell-Boltzmann distribution of molecular speeds and important quantities derived therefrom, such as the most probable speed, mean speed, and root-mean-square speed. The crucial step in the derivation of this distribution from the results developed in the last lecture is the transformation of the velocity phase-space volume element into spherical polar coordinates. This is introduced by use of a geometrical construction to relate the speed to the velocity components, and the independence of the velocity components introduced in the previous lecture is used to justify the equivalence of all directions and the combination of all velocity-space volume elements into a spherical shell of volume $4\pi v^2 dv$. The formal relation between the volume elements in cartesian and polar coordinates is also stated (without the rather tedious proof) since it is also of importance in the later consideration of the statistical treatment of electric polarization, but for present purposes emphasis is placed on the intuitive argument. Finally, the distribution function is used to calculate the particular speeds mentioned above. (A supplementary handout provided with this lecture shows how the Gaussian integrals that arise in the analysis can be evaluated by fairly simple manipulations.)

Lecture No. 7

The properties of the Maxwell-Boltzmann speed distribution are expanded upon here, and the distribution of energies is derived. Particular emphasis is placed on the problem of estimating various cumulative probabilities, *viz.*, the probable fraction of molecules with a given component of velocity greater than some value, and the corresponding probabilities for the speed and energy. Tables of the higher transcendental functions (the error function and the gamma distribution) that are required for this purpose are provided. The discussion is commenced by drawing attention to the *incorrect* identification (commonly found in elementary general chemistry textbooks - see, *e.g.*, Pilar, 1979; Brady and Humiston, 1982) of the ordinate in the Maxwell-Boltzmann distribution as the probable fraction of molecules with speed v: this confuses the fundamental concepts of a cumulative probability and a probability density. Attention is first devoted to the cumulative distribution of the individual velocity components, which is expressed in terms of the error function. Integration by parts is used to obtain the corresponding cumulative probability for the speed, and finally this is transformed to the distribution of molecular energies (expressible in terms of the gamma distribution). The change in the shape of these distribution functions with increasing temperature is used to reinforce the conclusions from Lecture No. 4, regarding the effect of temperature on the entropy. Finally, the distribution functions are used to determine the flux of molecules across a plane, and to derive the ideal gas equation of state.

Lecture No. 8

The Statistical Thermodynamics of molecules possessing rotational and vibrational degrees of freedom is introduced by posing the question, 'In our analysis of the distribution of molecular speeds and associated kinetic energy of a monatomic gas, what we found was that the average kinetic energy per mole was $3R/2$, irrespective of the mass of the molecule. Do you think that the average energy resulting from rotational and vibrational motion is also independent of molecular characteristics (such as moments of inertia and bond force constants)?' Attention is then turned to the construction of a classical expression for the total energy of a diatomic molecule in which the harmonic approximation is used, leading to the result that this energy depends quadratically on seven coordinates. With this in hand, the partition function is evaluated by straightforward application of the Gaussian integrals used in Lectures 6 and 7, leading to the result that the molar internal energy is $RT/2$ for each component of the molecular energy that depends quadratically on some coordinate. Finally, this is summarised by a formal statement and proof of the Equipartition Principle, and the continuous dependence of energy on coordinates is identified as the essential underlying assumption.

Lecture No. 9

Essential physical differences between classical and quantum treatments of molecular motion are noted, in particular the Heisenberg Uncertainty Principle and the origin of discrete energy levels from the boundary conditions imposed on the wave functions. The focus question here is, 'How can the Uncertainty Principle be expected to be relevant in the specification of microstates and the evaluation of partition functions?' The expression for the allowed energy levels for a particle in a box is then stated and the partition function evaluated. Reference to the Uncertainty Principle then allows the nondimensionalizing factor in the classical partition function to be identified as the smallest possible element of position-momentum phase space in which a molecule can be said to be located. The internal energy is worked out and compared with the classical treatment. The same procedure is then applied to the rigid diatomic rotator and simple harmonic oscillator. The assumption implicit in approximating the sums in the translational and rotational partition functions by integrals is identified, and the connexion between this assumption and the applicability of classical models is noted.

Lecture No. 10

The purpose of this lecture is to develop the idea of the physical significance of the partition function as a quantitative measure of the volume of phase space effectively accessible to a particle. The focus question is, 'How do you think that the separation between energy levels affects the value of a partition function?', and is directly connected with the exercise done in Lecture 4. Attention is first focussed on the translational partition function for a particle in a box, as expressed in terms of the volume divided by the cube of the thermal wavelength. A rough calculation of a typical thermal wavelength is made and used to rationalise the huge values typically obtained for this partition function. The effect of the dimensions of the container on the separation of the energy levels is determined by estimating the separation between the quantum states and comparing this with kT for a cavity of dimension 1 nm, and repeating this comparison for a container of dimension 0.1 m. This exercise is designed to lead to the conclusion that increasing the size of the container reduces the energy level separation compared with kT, thereby increasing the number of quantum states (*i.e.*, the volume of momentum phase space) accessible to a particle. Next, the evaluation of the rotational partition function is considered by introducing the concept of the rotational temperature, and the errors involved in the replacement of the summation by an integral are estimated by use of the Euler-Maclaurin formula (a table of the series for arguments greater than 0.01 is given). Finally, the use of the characteristic vibrational temperature in evaluating vibrational partition functions is demonstrated.

Statistical Thermodynamics Lecture No. 1

From the earliest stages of our study of chemistry, the behaviour of matter is explained to us in terms of various molecular models. When we come to the study of thermodynamics, we find that the main aim is to derive general relations describing the energetics of the transformations of substances - the generality of these results requires that they be derived largely *without* assuming a molecular model of matter. The purpose of statistical thermodynamics is to achieve a synthesis of these two viewpoints, *i.e.*, to predict thermodynamic properties of matter from a molecular model.

Since most molecules are massive enough to be described with reasonable accuracy by classical mechanics, we could expect in principle to determine the positions and velocities of each molecule as a function of time by solution of Newton's equations of motion. While this is computationally feasible for collections of a few hundred molecules, it is completely out of the question for macroscopic quantities of matter. The unimaginably huge numbers of molecules in real physical systems compels us to adopt a *statistical* approach, in which we relate thermodynamic observables to average properties of molecules.

The atoms or molecules in a substance are in ceaseless motion, but at any instant of time we can in principle characterise the state of the substance by a set of particle positions and momenta, which we refer to as a *microstate*. Each microstate is characterised by an *energy*. We seek to describe the substance by determining the relative importance of microstates of a given energy.

There are two ways in which this can in principle be done. One way is to observe the system for a sufficiently long time, and see how much time it spends in microstates with a given energy. The other way is to imagine a a collection of copies of the system - called an ensemble - sufficiently large in number that each possible microstate is represented at least once. If the members of the ensemble are in thermal contact with each other but prevented from exchanging matter (a *canonical ensemble*), we can expect a distribution of energies to be established, in which relatively few systems are in microstates with very high or very low energies. The determination of this distribution is the central goal of statistical thermodynamics. The time-average and ensemble-average descriptions of the system are generally assumed to be equivalent: this assumption is referred to as the *ergodic hypothesis.*

If the members of the ensemble are assumed to be thermally as well as mechanically isolated from each other (*i.e.*, we have a *microcanonical ensemble*), what can we say about the distribution of microstates? The answer is 'nothing' - all we can do is to make the *assumption* that in a microcanonical ensemble *microstates of the same energy are equally probable*. This assumption is called the *postulate of equal a priori probabilities*. It is not provable, but it is retained because the predictions of statistical mechanics have been shown to be in good agreement with experiment.

To proceed further with the development of a statistical model of matter, we need to introduce some fundamental concepts from statistics and probability. The most important of these concepts is that of a *distribution function*, or *probability density*, which enables us to determine the probability that some random variable x will have an energy lying in some specified range. (In the statistical-mechanical context, this random variable is molecular energy or some coordinate on which the energy depends, but at the present point it is not necessary to be more specific than this.) The distribution function $f(x)$ is defined so that the probability that x lies between x and $x + dx$ is $f(x)dx$. The probability of finding a value of x between x_1 and x_2 is therefore given by an integral of the probability density:

$$P(x_1 \le x \le x_2) = \int_{x_1}^{x_2} f(x)\,dx. \tag{1}$$

For the probabilities to be meaningful, the distribution function must be *normalised, i.e.*

$$P(-\infty < x < \infty) = \int_{-\infty}^{\infty} f(x)\,dx = 1. \tag{2}$$

This simply says that any value of x must have some probability. The *average* or *expectation* value of x is given by

$$<x> = \int_{-\infty}^{\infty} x\,f(x)\,dx. \tag{3}$$

We shall also require the concept of *statistical independence*. If two events are independent, the probability that both will occur simultaneously is given by the *product* of the individual probabilities. For example, in a gas of non-interacting particles, the energy possessed by one particle is *independent* of the energy possessed by another. If we let $f(E_1)$ be the probability that particle 1 has energy E_1 and $f(E_2)$ be the probability that particle 2 has energy E_2, then the probability that the pair of particles has an energy $E_1 + E_2$ is $f(E_1)f(E_2)$.

We can use the above statistical concepts to derive the form of the energy distribution function for a gas of noninteracting particles. The starting point is the functional equation that results from the statistical independence of the energies of two particles:

$$f(E_1 + E_2) = f(E_1)f(E_2) \tag{4}$$

If we differentiate the left-hand side of this equation partially with respect to either E_1 or E_2, we get the same result:

$$\frac{\partial f(E_1 + E_2)}{\partial E_1} = \frac{df(E_1 + E_2)}{d(E_1 + E_2)}.\,1 = \frac{\partial f(E_1 + E_2)}{\partial E_2}. \tag{5}$$

This means that the results of similar differentiation of the other sides of the functional equation must also be equal:

$$f'(E_1)f(E_2) = f(E_1)f'(E_2). \tag{6}$$

Division of both sides of this equation by $f(E_1)f(E_2)$ results in:

$$\frac{f'(E_1)}{f(E_1)} = \frac{f'(E_2)}{f(E_2)} = \beta', \tag{7}$$

where β' is a constant. The solution to this equation is

$$f(E) = \alpha e^{\beta' E}, \tag{8}$$

where α is another constant, which can be determined by the normalisation condition. If the *degeneracy* or statistical weight of each state of energy E is denoted by $g(E)$, normalization requires that

$$\int_0^{\infty} g(E)f(E)\,dE = \alpha\int_0^{\infty} g(E)e^{\beta' E}dE = 1 \tag{9}$$

This integral can be expected to exist only if β' is negative, so we write $\beta' = -\beta$ where $\beta > 0$, and

$$\alpha = \frac{1}{z}, \qquad \text{where} \qquad z = \int_0^\infty g(E)e^{-\beta E}dE \tag{10}$$

is known as the *partition function.* Where the particles in the system are restricted to discrete energies, the partition function involves a summation rather than an integral:

$$z = \sum_{i=1}^{\infty} g_i\, e^{-\beta E}. \tag{11}$$

The resulting distribution of molecular energies is referred to as the Boltzmann Distribution. In either the discrete or continuous case it is clear from the above analysis that the significance of the partition function is in ensuring that the probabilities of the accessible energy states sum to unity. Furthermore, as we shall see in subsequent lectures, all the thermodynamic functions can be expressed in terms of the partition function.

Learning Objectives

Knowledge

1.1.1 Define the terms 'canonical ensemble' and 'microcanonical ensemble'.

1.1.2 State the ergodic hypothesis and the principle of equal *a priori* probabilities.

1.1.3 State the relation between the probability of the simultaneous occurrence of two statistically-independent events in terms of the individual probabilities.

1.1.4 State the normalization condition that must be satisfied by a probability density function.

1.1.5 State the formula for the expectation value of a quantity in terms of its probability density.

Comprehension

1.2.1 Show how the assumption of statistical independence of molecular energies in a system of noninteracting particles leads to a functional equation for the distribution function.

1.2.2 Explain the significance of the normalization condition and the expectation value obtained from a probability density.

Application

Given a probability density function, work out

1.3.1 the normalization constant.

1.3.2 the expectation value by application of the general formula.

Analysis

1.4.1 Derive the Boltzmann Distribution by transformation of the functional equation into a differential equation and applying the normalization condition, for systems of noninteracting particles that can assume either continuous or discrete energies.

Example: Properties of Distribution Functions

We consider here an example illustrating the operation of the fundamental properties of distribution functions that we shall be using many times in our consideration of the applications of statistical thermodynamics. The particular example has nothing to do with statistical thermodynamics, but is chosen merely because the functions involved are quite simple and can be dealt with by elementary calculus.

A random variable is said to have a Cauchy distribution if its probability density function is given by

$$f(x) = \frac{k}{a^2 + x^2}, \qquad \text{for } -\infty < x < \infty. \tag{12}$$

(a) Express k in terms of a by application of the normalization condition.
(b) Determine the expectation value of x.
(c) Find expressions for: the cumulative probability distribution (*i.e.*, the probability that x is less than some value x_0); its complement (*i.e.*, the probability that x is greater than some value x_0), and the probability that x lies between x_1 and x_2.
(d) Sketch graphs of f, and the cumulative distribution function and its complement as a function of x_0/a.

(a) We note that since the given function is even (*i.e.*, $f(x) = f(-x)$), application of the normalization condition yields

$$\int_{-\infty}^{\infty} f(x)\, dx = 2\int_{0}^{\infty} f(x)\, dx = 1. \tag{13}$$

The integral involved here can be evaluated by elementary methods (substitution of $x = a \tan \theta$) or looked up in a table of integrals:

$$\int_{0}^{\infty} \frac{k}{a^2 + x^2}\, dx = k\left[\frac{1}{a}\tan^{-1}\left(\frac{x}{a}\right)\right]_0^{\infty} = \frac{\pi k}{2a}. \tag{14}$$

Therefore,

$$k = \frac{a}{\pi} \qquad \text{and} \qquad f(x) = \frac{a/\pi}{a^2 + x^2} = \frac{1}{\pi a\left(1 + \frac{x^2}{a^2}\right)}. \tag{15}$$

(b) The expectation value of x is

$$\int_{-\infty}^{\infty} x f(x)\, dx = \frac{1}{\pi a}\int_{-\infty}^{\infty} \frac{x}{\left(1 + \frac{x^2}{a^2}\right)}\, dx = 0, \tag{16}$$

This is so because the integrand is an odd function of x; the integrals from 0 to some finite value x_0 and from 0 to $-x_0$ are equal and opposite, for all values of x_0. For a symmetrical function such as this one it is intuitively reasonable to expect the mean value to lie exactly at the midpoint of the graph.

(c) The cumulative probability distribution is

$$P(-\infty < x \le x_0) = \frac{a}{\pi}\left[\frac{1}{a}\tan^{-1}\left(\frac{x}{a}\right)\right]_{-\infty}^{x_0} = \frac{1}{2} + \frac{1}{\pi}\tan^{-1}\left(\frac{x_0}{a}\right), \tag{17}$$

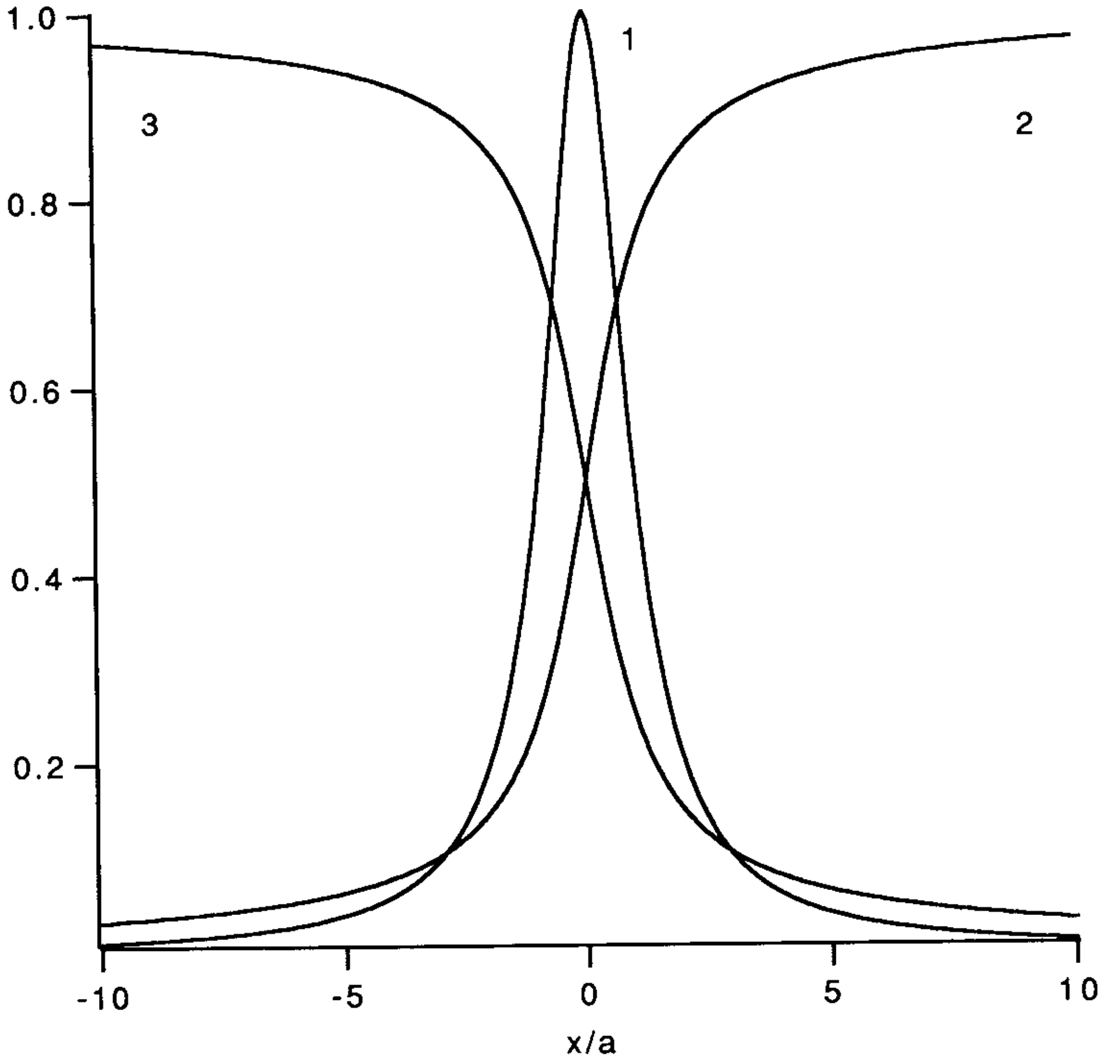
so that the complementary function is

$$\begin{aligned} P(x_0 \le x < \infty) &= 1 - P(-\infty < x \le x_0) \\ &= \frac{1}{2} - \frac{1}{\pi}\tan^{-1}\left(\frac{x_0}{a}\right). \end{aligned} \tag{18}$$

From these results, the probability of finding a value of x between x_1 and x_2 is

$$P(x_1 \le x \le x_2) = \frac{1}{\pi}\left[\tan^{-1}\left(\frac{x_2}{a}\right) - \tan^{-1}\left(\frac{x_1}{a}\right)\right]. \tag{19}$$

(d) The graphs of the required functions are as follows. Curve 1: $\pi a f(x)$; curve 2: $P(x < x_0)$; curve 3: $P(x > x_0)$.



Exercises on Distribution Functions

1. A random variable n has a probability density given by

$$f(n) = C\,e^{-a-bn}, \quad n = 0,1,2,\ldots$$

where a and b are positive constants. Determine the constant C in terms of a and b, and calculate the expectation value of n. Sketch a graph of this expectation value as a function of the parameter b, assuming that $a = 0$.
[Hint: you might find the identities

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \qquad \sum_{n=1}^{\infty} n x^{n-1} = \frac{1}{(1-x)^2}$$

to be useful.]

2. A random variable is restricted to the two possible values $n = \pm 1$, according to the probability density given by

$$f(n) = C\,e^{pn}$$

where p is a positive parameter and C is a normalisation constant. Determine C , and sketch a graph of the expectation value from the normalised density function as a function of p.

3. A random variable is said to have a Weibull distribution if its probability density is given by

$$f(x) = k x^{\beta-1} e^{-\alpha x^{\beta}},$$

where $x > 0$ and α and β are positive parameters.

(i) Express k in terms of α and β.

(ii) For $\beta = 2$ and $\alpha = 1$, draw a graph of the normalised probability density and the corresponding cumulative distribution.

[The following results might be useful in working out the integral appearing in the cumulative distribution:

$$\frac{d}{dx}(x^{\beta}) = \beta x^{\beta-1}, \qquad \int f[u(x)]\frac{du}{dx}\,dx = \int f(u)\,du.]$$

4. Find the normalization constant and the expectation value of a random variable x characterised by the probability density

$$f(x) = C\,e^{px}$$

where x can vary continuously between -1 and 1, and p is a positive parameter. Find the normalising constant and plot the expectation value as a function of p. Compare your result with your answer to Problem 2. [The following integral will be of use:

$$\int x\,e^{px}\,dx = \frac{1}{p}\left(x - \frac{1}{p}\right)e^{px}].$$

Statistical Thermodynamics Lecture No. 2

In the previous lecture we saw how the Boltzmann distribution function could be derived in a simple way from the assumption that the energies possessed by two members of an ensemble are statistically independent. We now consider a more general and rigorous derivation that serves to illustrate another important property of the Boltzmann distribution - that it is the most probable distribution consistent with the constraints that the number of members and the total energy of the ensemble are both fixed.

The starting point in this alternative derivation is the assumption that the ensemble consists of N_1 systems distributed in microstates with energy $E_1,...,N_N$ particles in states with energy E_N. We are faced with the problem of determining the number of ways in which such a distribution can be constructed. By application of combinatorial analysis (see Further Information), the number of ways of distributing the systems among the states is readily shown to be

$$\Omega = \frac{(N_1 + N_2 + ... + N_N)!}{N_1!N_2!...N_N!} \qquad (1)$$

We can identify the probability of a given set of Ns with the number of ways in which it can be constructed. For example, one can imagine a situation in which nearly all of the systems are in the lowest possible energy state and the remainder are in an extremely high state, with none in states of intermediate energy. This is intuitively very much less probable than one in which intermediate states are occupied, and can be realised in a great deal fewer possible ways. We can therefore identify the required distribution as that which gives the *maximum* value of ln Ω.

In general, the maximum value of a function of several variables can be found by differentiating the function partially with respect to each variable and setting the result equal to zero. In this situation, the variables concerned are the occupation numbers N, but it is to be observed that the Ns cannot be varied independently - if we increase one of the Ns we do so at the expense of at least one other. We must therefore identify the state of the system as the most probable set of Ns, consistent with a constant total number of particles and constant total energy of the system. These constraints can be expressed by the equations

$$\sum_i N_i = N_T \quad \text{or} \quad \sum_i N_i - N_T = 0 \qquad (2)$$

$$\sum_i N_i E_i = E_T \quad \text{or} \quad \sum_i N_i E_i - E_T = 0 \qquad (3)$$

The constrained maximum of ln Ω is found by use of Lagrange's method of undetermined multipliers, which involves finding the maximum value of a new *objective function* F defined by

$$\mathrm{F} = \ln\Omega + \alpha(\sum_i N_i - N_T) + \beta(\sum_i N_i E_i - E_T) \qquad (4)$$

where α and β are constant parameters. The general idea is to express the set of Ns that maximises F in terms of these parameters and then to find values of the parameters by application of the constraints. To proceed further, we need a way of evaluating the factorials of the huge numbers present in the numerator and denominator of Ω. This is provided by Stirling's formula:

$$\ln N! \simeq N \ln N - N \quad \text{or} \quad N! \simeq (\frac{N}{e})^N. \qquad (5)$$

Therefore

$$\begin{aligned}\ln \Omega &= N_T \ln N_T - N_T - [N_1 \ln N_1 - N_1] - [N_2 \ln N_2 - N_2] - \ldots\ldots \\ &= N_T \ln N_T - N_1 \ln N_1 - N_2 \ln N_2 - \ldots\ldots - N_N \ln N_N\,; \qquad (6)\end{aligned}$$

the error associated with the use of Stirling's formula for sufficiently large numbers is negligible. To find the Ns for which F is a maximum we differentiate F partially with respect to each N and set the result to zero; this gives a set of N_T simultaneous equations. This is not nearly as complicated as one might suppose, since each equation involves only one N. Thus when $\ln \Omega$ is differentiated partially with respect to N_j, the only nonzero term is

$$\frac{\partial}{\partial N_j}(N_j \ln N_j) = N_j \cdot \frac{1}{N_j} + 1.\ln N_j = \ln N_j + 1 \simeq \ln N_j \qquad (7)$$

where again the error here is insignificant. Differentiation of F with respect to N_j therefore produces

$$\ln N_j + \alpha + \beta E_j = 0 \qquad \text{or} \qquad N_j = e^{-\alpha-\beta E_j},\ j = 1,2,3,\ldots,N \qquad (8)$$

We can determine the constant α by applying the finite size constraint expressed by equation 2:

$$\sum_j N_j = e^{-\alpha} \sum_j e^{-\beta E_j} = N_T$$

$$e^{-\alpha} = \frac{N_T}{\sum_j e^{-\beta E_j}} \qquad (9)$$

The probability of a state with energy E_j is therefore:

$$P(E_j) = \frac{N_j}{N_T} = \frac{e^{-\beta E_j}}{\sum_i e^{-\beta E_i}} \qquad (10)$$

The sum in the denominator is immediately recognisable as the partition function for a system restricted to discrete energy levels. We shall see that the thermodynamic properties of the system can all be calculated from a knowledge of this quantity. In general, we expect many states to have the same energy, so that the sum in the partition function contains groups of identical terms. We can therefore rewrite the partition function as a sum over energy levels rather than states, accounting for the identical terms by including a *degeneracy* or *statistical weight* g_k:

$$Z = \sum_k g_k e^{-\beta E_k} \qquad (11)$$

The distribution function in its present form expresses all occupation probabilities in terms of the remaining Lagrange multiplier β. We can see from the requirement that the argument of an exponential must be dimensionless that β has the dimensions of energy, but to identify it more specifically we have to apply the theory to this simplest possible physical system - the classical monatomic perfect gas.

Learning Objectives

Comprehension

2.2.1 Identify the formation of a distribution of ensemble members among energy states as a combinatorial problem.

2.2.2 Explain the relationship between the probability of a state and the number of ways it can be realised.

2.2.3 Explain the lack of independence of the numbers of systems in each subgroup.

2.2.4 Describe the constraints to be satisfied by the Ns that maximise the value of $\ln \Omega$.

Application

2.3.1 Estimate factorials of large numbers by use of the Stirling approximation.

Analysis

2.4.1 State the conditions that must be satisfied by the constrained maximum of $\ln \Omega$ according to the the Lagrange method of undetermined multipliers.

2.4.2 Show how the Boltzmann distribution arises by logarithmic differentiation of the objective function F.

2.4.3 Demonstrate the relationship between the Lagrange multiplier α and the partition function, in terms of the normalization of the distribution.

Further Information: Combinatorial Analysis

Combinatorial Analysis is based on a result known as the fundamental principle of counting, which states that if one decision can be made in n ways, and another decision can be made in m ways, the total number of ways that both decisions can be made is mn. For example, if we are interested in enumerating the possible *permutations* or sequences of n objects, the position of the first object can be selected in n ways, that of the second in $n - 1$ ways, and so on, until finally there is only one position possible for the last object. The total number of such sequences is therefore $n! = n(n-1)(n-2)...3.2.1$. If the objects are to be taken in small groups of r, the number of possible permutations is

$$P_r^n = n(n-1)(n-2)(n-3)...(n-r+1) = \frac{n!}{(n-r)!}.$$

If we are not interested in the *order* in which the objects in each small group are arranged, we have to divide this number by the number of permutations of r objects. The number of combinations is

$$C_r^n = \frac{P_r^n}{r!} = \frac{n!}{(n-r)!r!}.$$

The generalised form of this result that describes the number of combinations of n objects in p groups containing $r_1, r_2, r_3, ..., r_p$ members, such that $r_1 + r_2 + r_3 + ... + r_p = n$, is

$$\frac{(r_1 + r_2 + r_3 + ... + r_p)!}{(r_1)!(r_2)!...(r_p)!}$$

This is simply the total number of possible permutations of all the objects, divided by the number of permutations possible within each subgroup. In our case, the objects are the members of the ensemble, and the groups are the states. The intention of the above remarks is to familiarise you with the ideas that are relevant to the statistical mechanical problem - much more detailed discussions of combinatorial theory may be found in any good textbook on probability and statistics.

Further Information: Stirling's Approximation

Stirling's formula can be derived quite simply by observing that the log of a factorial is the sum of the logs of the factors:

$$\ln n! = \ln n + \ln(n-1) + \ln(n-2) + \dots + \ln 3 + \ln 2 + \ln 1.$$

The sum of all these logs can be approximated by an integral

$$\sum_{k=1}^{n} \ln k \simeq \int_1^n \ln x \, dx$$

which can be readily evaluated by integration by parts:

$$\begin{aligned}\int_1^n \ln x \, dx = \int_1^n \ln x \frac{dx}{dx} dx &= [x \ln x]_1^n - \int_1^n x \frac{d}{dx}(\ln x) \, dx \\ &= n \ln n - 1 \ln 1 - \int_1^n 1 \, dx \\ &= n \ln n - n + 1\end{aligned}$$

Since 1 is negligible in comparison with the sort of numbers we are interested in, we obtain the desired result:

$$\ln n! \simeq n \ln n - n.$$

Exercise:

Find a table of factorials in a mathematical handbook, and compare the results given with those obtained from Stirling's formula.

Statistical Thermodynamics Lecture No. 3

We have so far seen how the Boltzmann distribution can be derived in two different ways that each offer a different perspective on the fundamental problem of determining the energy distribution. In the first, the crucial assumption was seen to be that the energies of members of the ensemble are statistically independent random variables, and in the second, the distribution was shown to be the most probable arrangement consistent with a finite total size and energy of the ensemble. In each case, however, the significance of the partition function as a normalising constant is very clearly illustrated. We now consider the problem of establishing a connexion between the partition function and macroscopic thermodynamic functions.

For a system with allowed states of energy E_j and degeneracy g_j the formula for Z is

$$Z = \sum_j g_j e^{-\beta E_j} \tag{1}$$

We can determine an average energy by applying the formula for an expectation value:

$$<E> = \sum_j E_j g_j P(E_j) = \sum_j E_j \frac{g_j e^{-\beta E_j}}{Z}. \tag{2}$$

This can be related to Z by noting that

$$\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{1}{Z}\sum_j E_j g_j e^{-\beta E_j}. \tag{3}$$

We therefore obtain the result

$$<E> = -\frac{\partial \ln Z}{\partial \beta}. \tag{4}$$

This ensemble average energy can be identified as the internal energy of the system, U.

Identification of the other thermodynamic functions in terms of the partition function can be achieved by considering the dependence of Z on β and V, which, by the usual procedure for taking the total differential of a function of several variables, is expressed by

$$\begin{aligned} d(\ln Z) &= \left(\frac{\partial \ln Z}{\partial \beta}\right)_V d\beta + \left(\frac{\partial \ln Z}{\partial V}\right)_\beta dV \\ &= -U\,d\beta + \left(\frac{\partial \ln Z}{\partial V}\right)_\beta dV. \end{aligned} \tag{5}$$

We can write this in terms of the differential of U by observing that

$$d(\beta U) = U\,d\beta + \beta dU \quad \Rightarrow \quad -U\,d\beta = \beta\,dU - d(\beta U) \tag{6}$$

so that

$$dU = \frac{1}{\beta}d(\ln Z + \beta U) - \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial V}\right)_\beta dV. \tag{7}$$

Comparing this with the combined First and Second Laws of Thermodynamics:

$$dU = T\,dS - p\,dV \tag{8}$$

we can conclude that

$$T\,\mathrm{d}S = \frac{1}{\beta}\mathrm{d}(\ln Z + \beta U)$$

$$\text{i.e., } \frac{1}{\beta} = kT, \qquad \mathrm{d}S = k\,\mathrm{d}(\ln Z + \beta U) \tag{9}$$

where k is a constant independent of temperature, and

$$p = \frac{1}{\beta}\left(\frac{\partial \ln Z}{\partial V}\right)_{\beta}. \tag{10}$$

In terms of temperature and volume, our thermodynamic formulae can be written

$$U = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V \qquad p = kT\left(\frac{\partial \ln Z}{\partial V}\right)_T \qquad S = k\ln Z + \frac{U}{T} + \text{constant.} \tag{11}$$

Since the expression for S in equation 11 follows from integration of equation 9 we cannot avoid the constant of integration. If the (arbitrary) constant in the expression for the entropy is set equal to zero, as is reasonable if the Third Law of Thermodynamics is invoked, an expression can be derived for the Helmholtz function:

$$A = U - TS = -kT\ln Z. \tag{12}$$

In elementary treatments of thermodynamics, the entropy is often identified as a measure of the disorder or randomness in a system. We can illustrate this microscopic significance of the entropy very clearly by use of a statistical concept called the *uncertainty*, which can be used to characterise an experiment with many different possible outcomes, each of probability P_j:

$$H = -\sum_j P_j \ln P_j, \tag{13}$$

where the summation is over all possible outcomes. Clearly, this quantity is positive, since all the probabilities are less than 1. It can also be seen that H will be a maximum if all outcomes have equal probabilities. Intuitively, this corresponds to having a *minimum of information.* To apply this idea to statistical mechanics we regard this "experiment" as the assignment of the system to one of its possible microstates of energy E_j and use the Boltzmann distribution for the corresponding probability, with the result

$$-\sum_j P(E_j)\ln\left(\frac{e^{-\beta E_j}}{Z}\right) = \sum_j P(E_j)\ln Z + \sum_j E_j P(E_j)\beta = \ln Z + \beta U, \tag{14}$$

This is identical to the earlier expression for the entropy divided by k, if the integration constant is set equal to zero. Thus, the entropy is proportional to the statistical uncertainty of the system.It can be seen from this result that the thermodynamic state of the system is determined by the probabilities of *all possible microstates*. We can also see how this result arises from the earlier expression for the total degeneracy of the ensemble:

$$\Omega = \frac{N_T}{\prod_j N_j!}. \tag{15}$$

Taking logs and applying Stirling's approximation:

$$\ln \Omega = N_T \ln N_T - \sum_j N_j \ln N_j = -\sum_j N_j \ln \left(\frac{N_j}{N_T}\right), \tag{16}$$

since N_T is the number of systems in the canonical ensemble. The average contribution to the entropy per system is therefore obtained by dividing by N_T.This gives

$$\ln W = -\sum_j \left(\frac{N_j}{N_T}\right) \ln \left(\frac{N_j}{N_T}\right) = -\sum_j P(E_j) \ln P(E_j) \tag{17}$$

so that

$$S = k \ln W. \tag{18}$$

This famous formula is inscribed on the memorial to Ludwig Boltzmann in Vienna. It is clear from this result that when there is only *one* possible configuration of the system (as in a perfect crystal at absolute zero), the entropy is zero. This lends support to our earlier assumption that the integration constant in equation 11 could be set equal to zero. The physical implication of equation 18 is that the positive entropy associated with higher temperatures can be regarded as a measure of our lack of information about the molecular configuration of a system.

Learning Objectives

Knowledge

3.1.1 State the formula for the statistical uncertainty.

Comprehension

3.2.1 Explain why the ensemble average energy can be regarded as the internal energy.

3.2.2 Describe the behaviour of the uncertainty of an experiment in the limiting cases where there is only one possible outcome and where all outcomes are equally probable.

3.2.3 Describe how the uncertainty can be identified with the entropy of a system.

3.2.4 Describe the connexion between the statistical-mechanical definition of entropy and the Third Law of Thermodynamics.

Application

3.3.1 Calculate the difference in entropy between two configurations of a system characterised by different values of W.

Analysis

3.4.1 Demonstrate the equivalence of the definitions of U given by equations 2, 4, and 11.

3.4.2 Demonstrate the equivalence of the definitions of S given by equations 11 and 14.

3.4.3 Justify the steps in the derivations of equations 9, 11, 14, and 18.

Statistical Thermodynamics Lecture No. 4

The purpose of this lecture is to apply the formulae that we have derived to the simplest possible system - the classical monatomic perfect gas. Our purpose is not only to demonstrate the calculation of the thermodynamic functions, but more importantly, to identify the Boltzmann constant *k*.

We assume our system to consist of *N* atoms of mass *m*, confined to a volume *V* at temperature *T*. We further assume that these particles can be treated classically, *i.e.*, that they can assume a continuous range of kinetic energy. This second assumption is reasonable if the atoms are sufficiently massive that they can be described by Newton's equations of motion as opposed to the Schroedinger equation of quantum mechanics. (As we shall see in our later discussion of the statistical mechanics of quantum systems, quantum effects in gases possessing only translational degrees of freedom are negligible except under the most extreme conditions.) The energy of the system is therefore the sum of the kinetic energies of the atoms:

$$E = \sum_{j} \frac{1}{2} m \boldsymbol{v}_i^2, \tag{1}$$

where boldface type has been used to signify that the quantity represented is a vector. In terms of the components of a single velocity vector $\boldsymbol{v}_i$, we have

$$\boldsymbol{v}_i = (v_{ix}, v_{iy}, v_{iz}) \qquad \text{so that} \qquad \boldsymbol{v}_i^2 = \boldsymbol{v}_i \bullet \boldsymbol{v}_i = v_{ix}^2 + v_{iy}^2 + v_{iz}^2. \tag{2}$$

Each microstate of the system requires specification of the position and velocity of each atom, in terms of its position in the container and the values of its velocity components. There are evidently 6*N* independent variables or coordinates that have to be considered; the range of possible values of all these coordinates define the *phase space* of the system. To work out the partition function for the gas, it is necessary to integrate over all space coordinates and all values of the velocity components for each atom:

$$Z = \frac{1}{N! h_0^{3N}} \int_V \cdots \int_{-\infty}^{\infty} \exp[-\beta \sum_{i=1}^{N} \frac{1}{2} m \boldsymbol{v}_i^2] d\boldsymbol{r}_1 d\boldsymbol{v}_1 .... d\boldsymbol{r}_N d\boldsymbol{v}_N, \tag{3}$$

where the abbreviations

$$d\boldsymbol{r} = dx\, dy\, dz \qquad \text{and} \qquad d\boldsymbol{v} = dv_x\, dv_y\, dv_z$$

have been used, and h_0 is a factor that ensures that the partition function is dimensionless (we shall learn later in our treatment of quantum systems that this quantity is related to the minimum error with which we can specify simultaneously the position and momentum of a particle). The factor of *N*! results because the atoms are indistinguishable: the *N* individual energies can be permuted among the *N* atoms in *N*! ways. Major simplifications of this formidable-looking expression can be made by observing that the integrations over space and velocity coordinates are the same for all atoms. Therefore:

$$Z = \frac{z^N}{N!}, \tag{4}$$

where

$$z = \frac{1}{h_0^3} \int_V \int\int\int_{-\infty}^{\infty} \exp[-\beta \frac{m}{2}(v_x^2 + v_y^2 + v_z^2)] d\boldsymbol{r}\; dv_x dv_y dv_z.$$

Since the energy of the atoms is completely independent of the spatial coordinates, the integral over $d\boldsymbol{r}$ gives the volume of the container, and since the integrations over each velocity component can be performed separately and are all equal, we obtain

$$z = \frac{V}{h_0^3}\left[\int_{-\infty}^{\infty} \exp\left(-\frac{\beta m v_x^2}{2}\right) dv_x\right]^3. \qquad (5)$$

The integral over the velocity coordinate is the simplest of a class of expressions called Gaussian Integrals. In our later more detailed discussion of kinetic theory, we shall see that such integrals can in fact be evaluated by fairly simple methods, but for the present, we make use of the well-known result (that can be found in tables of definite integrals)

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}, \qquad \text{where } \alpha > 0. \qquad (6)$$

Therefore

$$z = \frac{V}{h_0^3}\left(\frac{2\pi}{\beta m}\right)^{3/2} = \frac{V}{h_0^3}\left(\frac{2\pi kT}{m}\right)^{3/2}, \qquad (7)$$

$$Z = \frac{V^N}{N!}\left(\frac{2\pi kT}{m h_0^2}\right)^{\frac{3N}{2}}, \qquad (8)$$

and

$$\ln Z = N \ln \left[\frac{V}{h_0^3}\left(\frac{2\pi kT}{m}\right)^{3/2}\right] - N \ln N + N. \qquad (9)$$

The thermodynamic functions can all be derived from ln Z. For example, the pressure is

$$p = kT\left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{NkT}{V}. \qquad (10)$$

This is identical with the ideal gas equation of state

$$p = \frac{nRT}{V} \qquad (11)$$

if we make the identification

$$k = \frac{R}{N_A}, \qquad (12)$$

where N_A is Avogadro's number. Another important result is the internal energy, which is

$$U = kT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V = \frac{3NkT}{2}, \qquad (13)$$

from which follows in turn the expression for the heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3Nk}{2} = \frac{3nR}{2}. \qquad (14)$$

Learning Objectives

Knowledge

4.1.1 Write the expression for the total energy of a monatomic perfect gas, in terms of the velocity vectors for each atom and the components of these vectors.

4.1.2 Identify the coordinates required for specification of each microstate of the gas.

Comprehension

4.2.1 Explain why the indistinguishability of the atoms leads to the factor of $N!$ in equation 4.

Analysis

4.4.1 Justify all the steps in the reduction of equation 3 to equation 8.

Evaluation of Gaussian Integrals

In statistical mechanics it is frequently of interest to evaluate integrals of Gaussian functions.

The simplest such Gaussian integral is

$$G_0 = \int_0^\infty \exp(-\alpha x^2)\, dx \tag{1}$$

Although there is no indefinite integral or antiderivative for the integrand, the above definite integral can be evaluated by a transformation of coordinates, as follows.

We consider first the double integral

$$I = \int_0^\infty\int_0^\infty \exp[-\alpha(x^2 + y^2)]\, dxdy \tag{2}$$

which we observe can be identified as the square of the integral of interest:

$$\int_0^\infty\int_0^\infty \exp[-\alpha(x^2 + y^2)]\, dxdy = (\int_0^\infty \exp(-\alpha x^2)\, dx)(\int_0^\infty \exp(-\alpha y^2)\, dy) \tag{3}$$

We next observe that the double integral I can be evaluated by transformation to polar coordinates:

$$x = r\cos\theta,\ y = r\sin\theta \tag{4a}$$

$$dx\, dy = r\, dr\, d\theta \tag{4b}$$

$$x^2 + y^2 = r^2 \tag{4c}$$

$$I = \int_0^\infty\int_0^{\pi/2} \exp(-\alpha r^2)\, r\, dr\, d\theta$$

$$= \frac{\pi}{2}\cdot\frac{1}{2\alpha}\int_0^\infty 2\alpha r\ \exp(-\alpha r^2)\, dr = \frac{\pi}{4\alpha} \tag{5}$$

From eq. 3, relating I to G_0, we then have

$$G_0 = \sqrt{I} = \int_0^\infty \exp(-\alpha x^2)\, dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}} \tag{6}$$

We next consider the evaluation of integrals of the form

$$G_{2n} = \int_0^\infty x^{2n} \exp(-\alpha x^2)\, dx \tag{7}$$

and

$$G_{2n+1} = \int_0^\infty x^{2n+1} \exp(-\alpha x^2)\, dx \tag{8}$$

The first class of these integrals can be obtained by differentiating with respect to α:

$$\int_0^\infty x^{2n}\exp(-\alpha x^2)\ \mathrm{d}x \ = \ (-1)^n \frac{\partial^n}{\partial\alpha^n}\int_0^\infty \exp(-\alpha x^2)\ \mathrm{d}x \qquad (9)$$

Therefore, using the above expression for the integral G_0:

$$G_2 \ = \ (-\frac{\partial}{\partial\alpha})\int_0^\infty \exp(-\alpha x^2)\ \mathrm{d}x \ = \ \frac{\sqrt{\pi}}{4\alpha^{3/2}} \qquad (10)$$

and generally,

$$G_{2n} \ = \ (-1)^n\frac{\partial^n}{\partial\alpha^n}(\frac{1}{2}\sqrt{\frac{\pi}{\alpha}}) \ = \ \frac{1.3.5....(2n-1)}{2^{n+1}}\sqrt{\frac{\pi}{\alpha^{2n+1}}} \qquad (11)$$

The first integral of the type in eq. (8) can be evaluated by usual integration methods:

$$G_1 \ = \ \int_0^\infty x\ \exp(-\alpha x^2)\ \mathrm{d}x \ = \ \frac{1}{2\alpha}\int_0^\infty 2\alpha x\ \exp(-\alpha x^2)\ \mathrm{d}x$$

$$= \frac{1}{2\alpha} \qquad (12)$$

As before, differentiation with respect to α introduces a factor of x^2 into the integrand:

$$G_3 \ = \ (-\frac{\partial}{\partial\alpha})\int_0^\infty x\ \exp(-\alpha x^2)\ \mathrm{d}x \ = \ \frac{1}{2\alpha^2} \qquad (13)$$

so that in general,

$$G_{2n+1} \ = \ (-1)^n\frac{\partial^n}{\partial\alpha^n}(\frac{1}{2\alpha}) \ = \ \frac{n!}{2\alpha^{n+1}} \qquad (14)$$

Statistical Mechanics Lecture No. 5

The purpose of this class is to illustrate the operation of the statistical-mechanical principles developed so far by working through a numerical example.

Exercise:
Considering a simple hypothetical system of particles that can be distributed among five equally-spaced energy levels given by

$$\varepsilon_j = (j - 1)\varepsilon, \qquad j = 1,2,3,4,5. \tag{1}$$

Calculate:
(i) the partition function
(ii) the occupation probability of each state
(iii) the internal energy in units of kT
(iv) the entropy in units of k
(v) the Helmholtz energy in units of kT

assuming that $\varepsilon/kT = 5, 1,$ and 0.1.

A. $\varepsilon/kT = 5.$

State	P.F. Term	Probability	Energy Term	Entropy Term
1				
2				
3				
4				
5				
Sum				

Helmoltz Energy/kT =

B. $\varepsilon/kT = 1.$

State	P.F. Term	Probability	Energy Term	Entropy Term
1				
2				
3				
4				
5				
Sum				

Helmoltz Energy/kT =

$\varepsilon/kT = 0.1$.

State	P.F. Term	Probability	Energy Term	Entropy Term
1				
2				
3				
4				
5				
Sum				

Questions:

1. In each case, plot a graph or histogram showing the probable fractions of particles in each state.

2. What trend do you observe in the entropy as a function of ε/kT ? Interpret this trend in terms of the information we have about the molecular configuration, as expressed by your answer to question 1.

3. How do the Internal Energy and Helmholtz function compare with the energies in each of these three situations?

Statistical Thermodynamics Lecture No. 6

From the partition function determined earlier for the classical perfect gas, we can determine the probability that a given molecule will have velocity components in specified ranges. In particular, the probability that a molecule will have *one* of its velocity components in a particular range is described by a density function obtained by integrating over all possible values of the other velocity components and the space coordinates. This is called the *marginal density function* and for (say) the x velocity component, and is defined by the equation

$$
\begin{aligned}
f_x(v_x)\,dv_x &= \frac{1}{z}\frac{1}{h_0^3}\int_V\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp(-\frac{m}{2kT}[v_x^2+v_y^2+v_z^2]\,dr\,dv_x dv_y dv_z \\
&= \frac{1}{z}\frac{V}{h_0^3}\left(\int_{-\infty}^{\infty}\exp[-\frac{mv_y^2}{2kT}]dv_y\right)\left(\int_{-\infty}^{\infty}\exp[-\frac{mv_z^2}{2kT}]dv_z\right)\exp[-\frac{mv_x^2}{2kT}]dv_x \\
&= \left(\frac{m}{2\pi kT}\right)^{1/2}\exp[-\frac{mv_x^2}{2kT}]dv_x. \qquad (1)
\end{aligned}
$$

which is the probability that a molecule has an x-velocity component between v_x and $v_x + dv_x$. We can see that this distribution function is correctly normalised since when it is integrated over all possible values of v_x, we obtain

$$\int_{-\infty}^{\infty} f_x(v_x)\,dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2}\int_{-\infty}^{\infty}\exp[-\frac{mv_x^2}{2kT}]\,dv_x = 1. \qquad (2)$$

We can also see that the expectation value of v_x, *viz.*,

$$\int_{-\infty}^{\infty} v_x f_x(v_x)\,dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2}\int_{-\infty}^{\infty} v_x\exp[-\frac{mv_x^2}{2kT}]\,dv_x = 0, \qquad (3)$$

since the integrand is an odd function. Identical results obviously apply to the other components. We can therefore conclude that the velocity components are normally distributed about a mean value of zero. The shape of this distribution is shown in Figure 1, for different values of the parameter $(kT/m)^{1/2}$. The distribution is seen to become broader for increasing temperature.

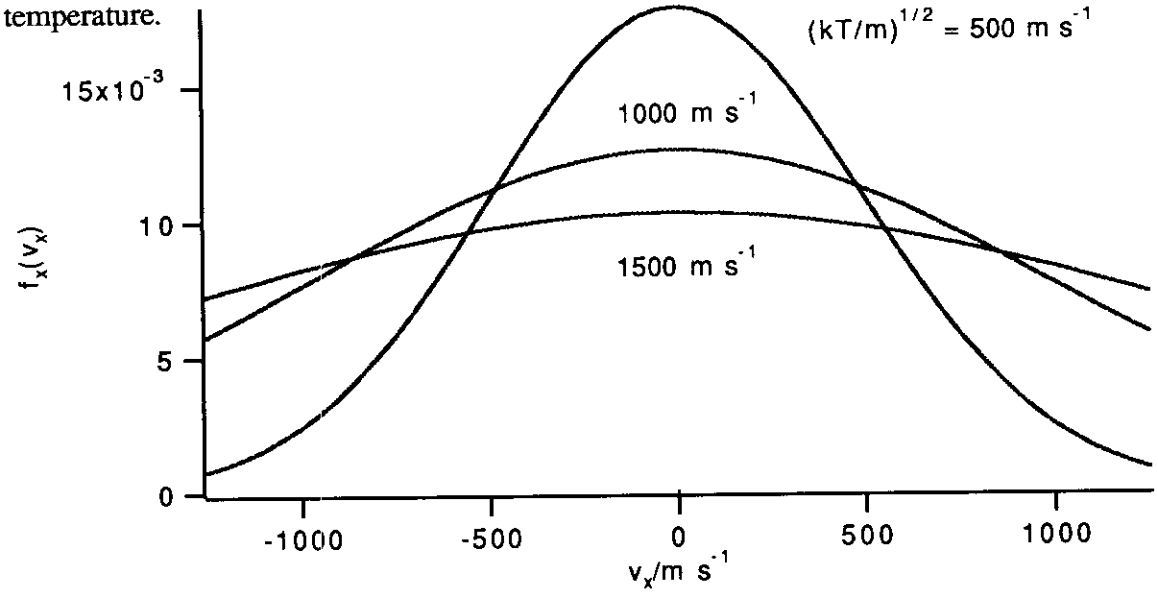


Figure 1: *Distribution functions for velocity components.*

While the motion of any particular molecule can be described by specifying its velocity components, it often proves more convenient to specify its *speed*, v, and the *direction* of motion. This direction is expressed in terms of two angles, θ and ϕ. The relation between the three velocity components v_x, v_y and v_z and the spherical polar coordinates v, θ and ϕ is expressed by the equations

$$v_x = v \sin\theta \cos\phi, \qquad v_y = v \sin\theta \sin\phi, \qquad v_z = v \cos\theta \tag{4}$$

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2}$$

and may be represented as in Figure 2:

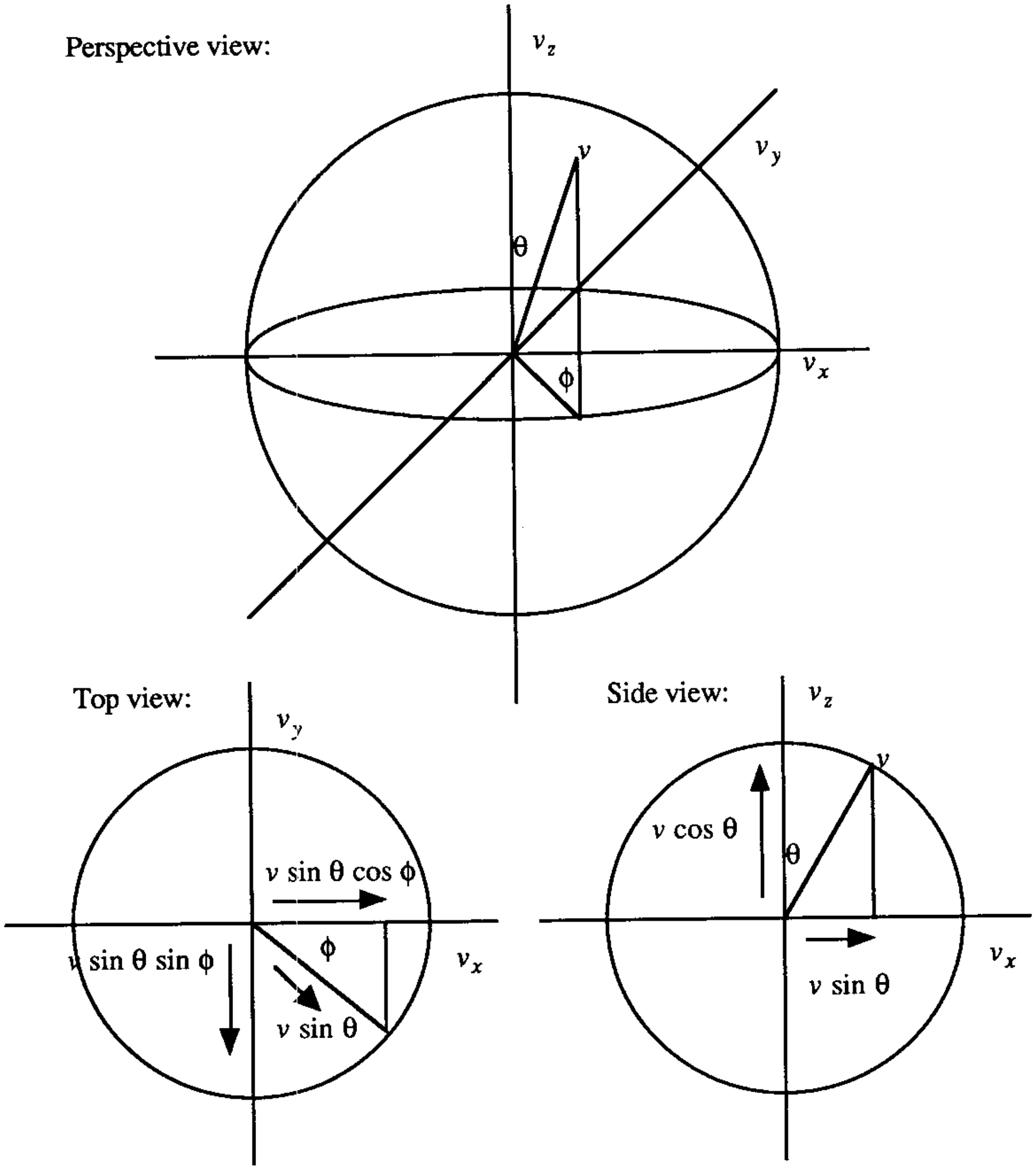


Figure 2: *Definition of polar coordinates.*

To transform the distribution function, it is necessary to rewrite the phase space volume element in terms of the polar coordinates. By tedious but straightforward manipulations that can be found in any textbook on advanced calculus, it can be shown that

$$dv_x dv_y dv_z = v^2 \sin\theta \, dv \, d\theta \, d\phi \tag{5}$$

From the diagrams given, it is clear that θ can vary between 0 and π and ϕ between 0 and 2π. The probability that a given molecule is in the phase space element $d\boldsymbol{r}d\boldsymbol{v}$ about $\boldsymbol{r}$ and $\boldsymbol{v}$ can therefore be written

$$\frac{h_0^3}{V}\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)\frac{d\boldsymbol{r}d\boldsymbol{v}}{h_0^3} = \frac{1}{V}\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)d\boldsymbol{r}d\boldsymbol{v}$$

$$= \frac{1}{V}\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)d\boldsymbol{r}\; v^2 \sin\theta \, dv \, d\theta \, d\phi.$$

In the absence of external potential fields, all positions in the container are equivalent, and all the directions corresponding to the angles θ and ϕ are equivalent by symmetry. The probability that a molecule possesses a speed between v and $v + dv$ is therefore

$$\left(\int_V \frac{d\boldsymbol{r}}{V}\right)\left(\int_0^{\pi} \sin\theta \, d\theta\right)\left(\int_0^{2\pi} d\phi\right) \exp\left(-\frac{mv^2}{2kT}\right) dv = \eta(v)\, dv,$$

where

$$\eta(v) \equiv 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right). \tag{6}$$

This function is known as the Maxwell-Boltzmann distribution of molecular speeds. The physical significance of the transformation used to obtain equation 6 can also be understood by observing that since the directions are all equivalent, the sum or integral of all polar velocity-space volume elements produces a spherical shell of area $4\pi v^2$ and thickness dv.

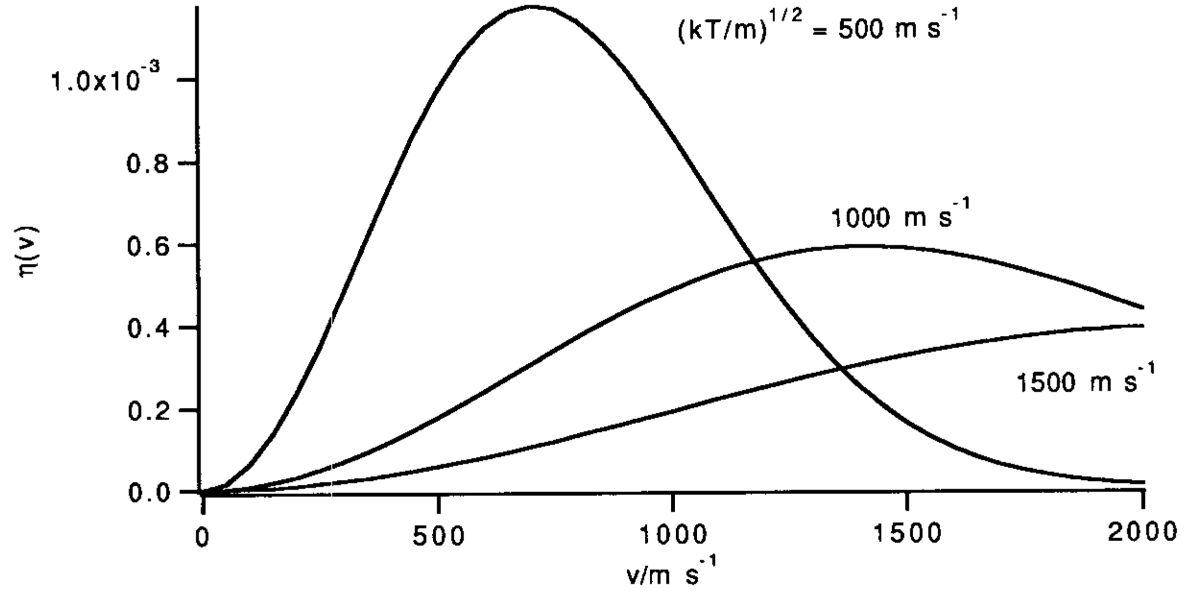


Figure 3: *Mawell distribution function for molecular speeds.*

The density functions shown in Figures 2 and 3 can both be characterised by an expectation value and a most probable value of the respective variable (velocity component or speed, respectively), *i.e.*, a value for which the density function has its maximum value. In the case of the velocity component function, it clear from the symmetry of the graph that the most probable value is the same as the expectation value. This is not the case for the distribution of speeds given by equation 6. The most probable speed is defined by the condition that

$$\frac{d\eta(v)}{dv} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)\left[2v - \frac{mv^3}{kT}\right] = 0,$$

or

$$v = v_m = \sqrt{\frac{2kT}{m}}. \qquad (7)$$

The expectation value or average speed is

$$<v> = \int_0^\infty v\,\eta(v)\,dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^3\exp\left(-\frac{mv^2}{2kT}\right)dv$$

$$= \sqrt{\frac{8kT}{\pi m}}. \qquad (8)$$

It is also possible to determine a mean-square speed:

$$<v^2> = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty v^4\exp\left(-\frac{mv^2}{2kT}\right)dv = \frac{3kT}{m},$$

so that the root-mean-square speed is

$$v_{\rm rms} = <v^2>^{1/2} = \sqrt{\frac{3kT}{m}}. \qquad (10)$$

All these characteristic speeds are seen to be directly proportional to the square root of temperature and inversely proportional to the molecular mass. We can express them all relative to v_m:

$$<v> = \frac{2}{\sqrt{\pi}}v_m \quad \text{and} \quad v_{\rm rms} = \sqrt{\frac{3}{2}}v_m. \qquad (11)$$

Mean speeds of gas molecules at 300 K are typically several hundred meters per second. For example, for a nitrogen molecule (mass 4.648×10^{-26} kg),

$$v_m = \sqrt{\frac{2 \times (1.380 \times 10^{-23}\ \mathrm{J\,K^{-1}}) \times (300\ \mathrm{K})}{(4.648 \times 10^{-26}\ \mathrm{kg})}} = 422.1\ \mathrm{m\,s^{-1}},$$

so that from equation 11 we obtain

$$<v> = \frac{2}{\sqrt{\pi}}v_m = 476.2\ \mathrm{m\,s^{-1}} \quad \text{and} \quad v_{\rm rms} = \sqrt{\frac{3}{2}}v_m = 516.9\ \mathrm{m\,s^{-1}}.$$

These speeds are approximately 1600 km/h or 1000 mph.

Learning Objectives

Knowledge

6.1.1 Define the marginal density function for a velocity component in terms of the partition function.

6.1.2 State the equation relating the differential volume elements of cartesian and spherical polar coordinates.

Comprehension

6.2.1 Describe the form of the marginal density function for each velocity component of a gas, and compare this with the form of the distribution of molecular speeds.

6.2.2 Demonstrate graphically the physical significance of the expectation value and most probable values from the density function.

6.2.3 Describe qualitatively how the transformation of the velocity-component distribution to polar coordinates leads to a velocity-space element that is a spherical shell of area $4\pi v^2$ and thickness dv.

Application

Calculate, according to the Maxwell-Boltzmann distribution of molecular speeds:

6.3.1 most probable speed.

6.3.2 the mean speed.

6.3.3 the root-mean-square speed.

Analysis

6.4.1 Derive the expressions for the most probable speed, mean speed and root-mean-square speed.

6.4.2 Derive the expressions for the marginal probability density functions of one and two velocity components.

6.4.3 Apply the distribution functions to evaluate expectation values for simple functions of the speed or velocity components.

Problems:

6.1 Calculate the most probable speed, the mean speed and the root-mean-square speed for methane molecules (molar mass 16.04 g/mol) at
(i) 300K;
(ii) 500K;
(iii) 1000K.

6.2 From the Maxwell-Boltzmann distribution function, estimate the probability that an oxygen molecule (molar mass 32.00 g/mol) will have a speed of 500 ± 1 m/s (*i.e.*, between 499 and 501 m/s) at 300 K. How does this speed compare with the mean speed at the given temperature?

6.3 At what temperature will the most probable speed in a gas of argon atoms (molar mass 39.95 g/mol) be 700 m/s?

6.4 In an earlier lecture, we arrived at the important result that the average kinetic energy in a monatomic perfect gas is $3kT/2$, irrespective of the atomic mass. By applying the definition of kinetic energy, show that this result also follows from our expression for the mean square speed according to the Maxwell-Boltzmann distribution.

6.5(i) Consider a gas of molecules (of molar mass 28 g/mol) at 300 K. Calculate the average kinetic energy per molecule and the root-mean-square speed.

(ii) Now suppose that the gas has suspended in it minute particles with molar mass 10 000 g/mol. What is the root-mean-square speed of these particles at this temperature?

Solutions

6.1 Use of the formulae requires the mass of the molecules in kg. This is

$$m = \frac{(16.04\ \text{g mol}^{-1}) \times (10^{-3}\ \text{kg g}^{-1})}{(6.02205 \times 10^{23}\ \text{mol}^{-1})} = 2.664 \times 10^{-26}\ \text{kg}.$$

Then:

$$v_m = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2 \times (1.38064 \times 10^{-23}\ \text{J K}^{-1}) \times (300\ \text{K})}{(2.664 \times 10^{-26}\text{kg})}} = 557.6\ \text{m s}^{-1},$$

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8 \times (1.38064 \times 10^{-23}\ \text{J K}^{-1}) \times (300\ \text{K})}{\pi \times (2.664 \times 10^{-26}\ \text{kg})}} = 629.2\ \text{m s}^{-1},$$

$$v_{\text{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3 \times (1.38064 \times 10^{-23}\ \text{J K}^{-1}) \times (300\ \text{K})}{(2.664 \times 10^{-26}\ \text{kg})}} = 683.0\ \text{m s}^{-1}.$$

At the other temperatures the answers are:

500 K: $v_m = 719.9\ \text{m s}^{-1}$; $\langle v \rangle = 812.3\ \text{m s}^{-1}$; $v_{\text{rms}} = 881.7\ \text{m s}^{-1}$;

1000 K: $v_m = 1018\ \text{m s}^{-1}$; $\langle v \rangle = 1149\ \text{m s}^{-1}$; $v_{\text{rms}} = 1247\ \text{m s}^{-1}$.

6.2 From the definition of $\eta(v)$, the required probability is

$$P \simeq \eta(v)\,\Delta v = 4\pi v^2\left(\frac{m}{2\pi kT}\right)^{3/2}\exp\left(-\frac{mv^2}{2kT}\right)\Delta v$$

$$= 4\pi \times (500\ \mathrm{m\ s^{-1}})^2 \times \left(\frac{5.314 \times 10^{-26}\ \mathrm{kg}}{2\pi \times (1.38064 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (300\ \mathrm{K})}\right)^{3/2}$$

$$\times \exp\left(-\frac{(5.314 \times 10^{-26}\ \mathrm{kg}) \times (500\ \mathrm{m\ s^{-1}})^2}{2 \times (1.38064 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (300\ \mathrm{K})}\right) \times (2\ \mathrm{m\ s^{-1}}) = 3.688 \times 10^{-3}.$$

6.3 We have

$$v_m = \sqrt{\frac{2kT}{m}} \qquad \text{or} \qquad T = \frac{mv_m^2}{2k}$$

$$T = \frac{(6.634 \times 10^{-26}\ \mathrm{kg}) \times (700\ \mathrm{m\ s^{-1}})^2}{2 \times (1.38064 \times 10^{-23}\ \mathrm{J\ K^{-1}})} = 1177\ \mathrm{K}.$$

6.4 The average molecular kinetic energy is related to the mean-square speed by

$$\langle\varepsilon\rangle = \langle\tfrac{1}{2}mv^2\rangle = \tfrac{1}{2}m\,\langle v^2\rangle.$$

Therefore

$$\langle\varepsilon\rangle = \frac{m}{2}\cdot\frac{3kT}{m} = \frac{3kT}{2},$$

in agreement with the result obtained directly from the classical partition function.

6.5(i) By application of the relevant formulae,

$$\langle\varepsilon\rangle = \frac{3kT}{2} = \frac{3 \times (1.38064 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (300\ \mathrm{K})}{2} = 6.213 \times 10^{-21}\ \mathrm{J},$$

$$v_{\mathrm{rms}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3 \times (1.38064 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (300\ \mathrm{K})}{(4.650 \times 10^{-26}\ \mathrm{kg})}} = 516.9\ \mathrm{m\ s^{-1}}.$$

(ii) Since the dispersed particles are in thermal (*i.e.* collisional) equilibrium with the gas molecules, their mean kinetic energy must be the same:

$$\langle\varepsilon\rangle = \tfrac{1}{2}mv_{\mathrm{rms}}^2 = 6.213 \times 10^{-21}\ \mathrm{J},$$

but their root-mean-square speed is much smaller:

$$v_{\mathrm{rms}} = \sqrt{\frac{2\langle\varepsilon\rangle}{m}} = \sqrt{\frac{2 \times (6.213 \times 10^{-21}\ \mathrm{J})}{(1.661 \times 10^{-23}\ \mathrm{kg})}} = 27.35\ \mathrm{m\ s^{-1}}.$$

Statistical Thermodynamics Lecture No. 7

In the previous lecture we derived the Maxwell-Boltzmann distribution function for a classical perfect gas and used it to estimate various average speeds. To obtain a more detailed picture of the distribution we need to consider the general problem of calculating the probability that a molecule has a velocity component or speed greater than some specified value. For example, the probability that a molecule has an x-component of its velocity greater than some value v_0 is given by

$$P(v_x > v_0) = \int_{v_0}^{\infty} f_x(v_x)\, dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} \int_{v_0}^{\infty} \exp\left(-\frac{mv_x^2}{2kT}\right) dv_x. \qquad (1)$$

We can't evaluate this integral in terms of elementary functions, but by putting

$$u = v_x\sqrt{\frac{m}{2kT}} \qquad dv_x = \sqrt{\frac{2kT}{m}}\, du \qquad (2)$$

we can simplify it to

$$P(v_x > v_0) = \frac{1}{\sqrt{\pi}} \int_{v_0\sqrt{\frac{m}{2kT}}}^{\infty} e^{-u^2} du \qquad (3)$$

$$= \frac{1}{2}\operatorname{erfc}\left(v_0\sqrt{\frac{m}{2kT}}\right),$$

where 'erfc' is the *complementary error function* defined by

$$\operatorname{erfc} x \equiv \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-u^2} du = 1 - \operatorname{erf} x, \qquad \text{and} \qquad \operatorname{erf} x \equiv \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-u^2} du.$$

The error functions may be evaluated by numerical integration or by various series expansions, and their values are tabulated in various mathematical handbooks. They are defined such that

$$\lim_{x\to\infty} \operatorname{erf} x = 1 \qquad \text{and} \qquad \lim_{x\to\infty} \operatorname{erfc} x = 0. \qquad (4)$$

We can appreciate the significance of the factor of 1/2 in equation 3 by recalling that because of the symmetry of the distribution function, we would obtain the same result for the probability that v_x is less than (*i.e.*, more negative than) - v_0. Thus, we can also write

$$P(|v_x| > v_0) = \operatorname{erfc}\left(v_0\sqrt{\frac{m}{2kT}}\right) \qquad (5)$$

for the probability that the *magnitude* of v_x is greater than v_0.

The probability that a molecule has a *speed* greater than v_0 is given by the integral of $\eta(v)$:

$$P(v > v_0) = \int_{v_0}^{\infty} \eta(v)\, dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_{v_0}^{\infty} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv. \qquad (6)$$

This can be simplified by recalling the definition of the most probable speed v_m and making the substitution $u = v/v_m$:

$$4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_{v_0}^{\infty} v^2 \exp\left(-\frac{mv^2}{2kT}\right) dv = \frac{4}{\sqrt{\pi}} \int_{v_0/v_m}^{\infty} u^2 e^{-u^2} du, \qquad v_m = \sqrt{\frac{2kT}{m}} \qquad (7)$$

The integral with respect to u can be expressed in terms of the error function by integration by parts:

$$\frac{4}{\sqrt{\pi}}\int_{v_0/v_m}^{\infty} u^2\, e^{-u^2} du \;=\; \frac{4}{\sqrt{\pi}}\,\{-\,\frac{1}{2}[u\, e^{-u^2}]_{v_0/v_m}^{\infty} \;+\; \frac{1}{2}\int_{v_0/v_m}^{\infty} e^{-u^2} du\,\}$$

$$=\; \frac{2}{\sqrt{\pi}}\,(\frac{v_0}{v_m})\, e^{-(\frac{v_0}{v_m})^2} \;+\; \mathrm{erfc}\,(\frac{v_0}{v_m}). \qquad (8)$$

The distribution of molecular ***energies*** can be determined from $\eta(v)$ by application of the relation between kinetic energy and speed:

$$E \;=\; \frac{mv^2}{2} \qquad v \;=\; \sqrt{\frac{2E}{m}} \qquad dv \;=\; \frac{dE}{\sqrt{2mE}} \qquad (9)$$

Therefore,

$$4\pi\,(\frac{m}{2\pi kT})^{3/2}\int_{v_0}^{\infty} v^2 \exp(-\,\frac{mv^2}{2kT})\, dv \;=\; 4\pi\,(\frac{m}{2\pi kT})^{3/2}\int_{E_0}^{\infty}\frac{2E}{m}\exp(-\,\frac{E}{kT})\,\frac{dE}{\sqrt{2mE}}$$

and after applying the substitution $u = E/kT$ and cancelling terms, the probability that the molecular energy is greater than $E_0 = mv_0^2/2$ is found to be

$$\mathrm{P}(E > E_0) \;=\; \frac{2}{\sqrt{\pi}}\int_{E_0/kT}^{\infty} u^{1/2} e^{-u}\, du \;=\; \int_{E_0}^{\infty}\zeta(E)\, dE, \qquad (11)$$

where the corresponding density function $\zeta(E)$ is defined by

$$\zeta(E) \;=\; \frac{2}{\sqrt{\pi}}\,\frac{E^{1/2}}{(kT)^{3/2}}\exp(-\,\frac{E}{kT}) \qquad (12)$$

and is shown in Figure 1 as a function of E/kT. The energy function has a vertical tangent at $E = 0$, as a result of the square root, in contrast to the corresponding function for the speeds, which is approximately parabolic when v is close to 0.

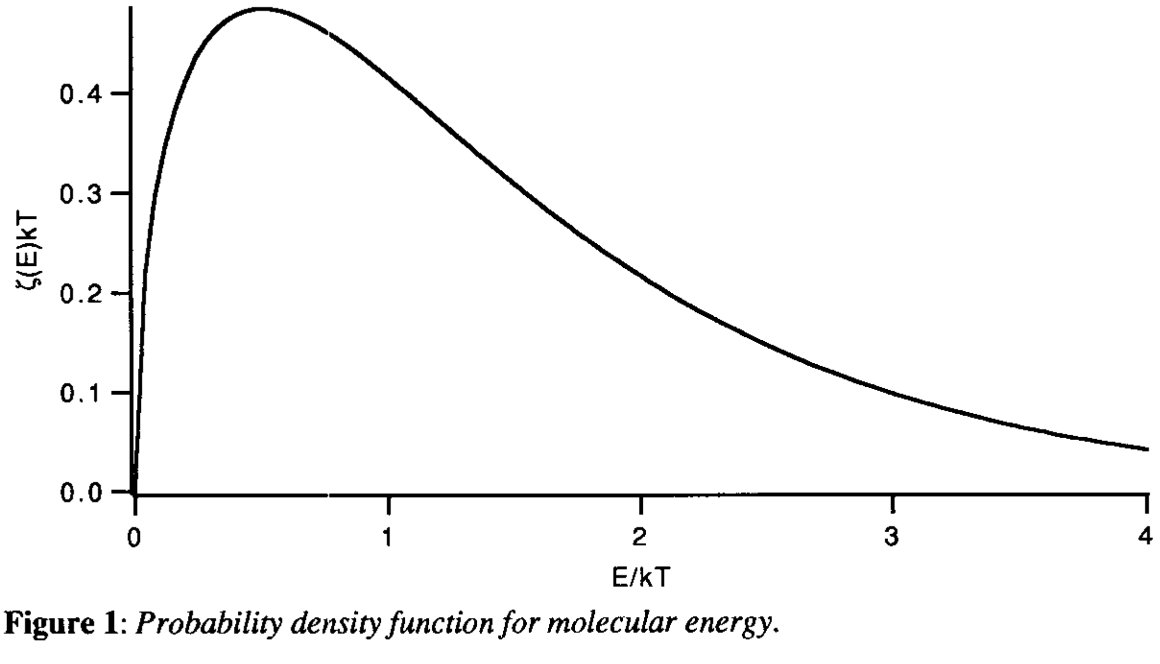


Figure 1: *Probability density function for molecular energy.*

We finally consider the problem of calculating the average velocity of molecules that are moving in a particular direction. From the symmetry of the velocity distribution, we can immediately say that the probability that a molecule will have a positive x-component of its velocity is 1/2. What we are interested in is the average value of the x-component of the velocity possessed by this half of the molecules. More specifically, we consider the average value of v_x over the range of values from 0 to infinity. This is given by

$$\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\int_0^\infty v_x \exp\left[-\frac{mv_x^2}{2kT}\right] dv_x\right)\left(\int_{-\infty}^{\infty} \exp\left[-\frac{mv_y^2}{2kT}\right] dv_y\right)\left(\int_{-\infty}^{\infty} \exp\left[-\frac{mv_z^2}{2kT}\right] dv_z\right)$$

$$= \left(\frac{m}{2\pi kT}\right)^{1/2}\int_0^\infty v_x \exp\left[-\frac{mv_x^2}{2kT}\right] dv_x = \sqrt{\frac{kT}{2\pi m}} = \frac{1}{4}<v>. \qquad (13)$$

Consider a molecule with a component of its velocity in the direction perpendicular to an element dA of the container (say, the x-direction). In a time interval dt, the distance travelled by the molecule defines a box of volume $(v_x dt)dA$. The number of molecules in this box is found by multiplying this volume by the number density, and the total number of molecules striking the surface dA in time dt is found by integrating over the distribution of all positive values of v_x. Since dt and dA are constants, this is equivalent to $(<v>/4)dAdt$. Dividing by $dtdA$, we find that the *flux* or total number of molecules striking unit area of the container per unit time is

$$J = \left(\frac{N}{V}\right)\frac{<v>}{4}. \qquad (14)$$

If we have an equimolar mixture of two gases, it is clear from this result and the expression derived earlier for the mean speed that the ratio of the fluxes of molecules is

$$\frac{J_2}{J_1} = \sqrt{\frac{m_1}{m_2}}. \qquad (15)$$

where m_1 and m_2 are the molecular masses.This result is known as *Graham's Law*.

A closely related problem is that of determining the pressure exerted by the gas. This is found by observing that each molecule with normal velocity component v_x transfers momentum $2mv_x$ to the surface. The momentum transfer from such molecules is

$$\text{(momentum change per molecule)} \times \text{(volume)} \times \text{(number density)}$$

$$= (2mv_x)\,(v_x dt\, dA)\,\left(\frac{N}{V}\right). \qquad (16)$$

The pressure can be identified as the total momentum transfer per unit area and unit time and is obtained by integrating this expression over the entire distribution of positive values of v_x and dividing by $dAdt$:

$$p = \left(\frac{N}{V}\right)\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\int_0^\infty 2mv_x^2 \exp\left[-\frac{mv_x^2}{2kT}\right] dv_x\right)\left(\int_{-\infty}^{\infty} \exp\left[-\frac{mv_y^2}{2kT}\right] dv_y\right)\left(\int_{-\infty}^{\infty} \exp\left[-\frac{mv_z^2}{2kT}\right] dv_z\right)$$

$$= \left(\frac{N}{V}\right)\left(\frac{m}{2\pi kT}\right)^{1/2} 2m\,\frac{\sqrt{\pi}}{4}\left(\frac{2kT}{m}\right)^{3/2} = \frac{NkT}{V}. \qquad (17)$$

This kinetic derivation of the ideal gas equation of state therefore makes rigorous the elementary interpretation of pressure as resulting from the collisions of molecules with the walls of their container.

Learning Objectives

Knowledge

7.1.1 State the formula for the probability that a molecule has a velocity component greater than some specified value.

7.1.2 Define the error function and complementary error function and identify their limiting values as the argument tends to infinity.

7.1.3 State the formula for the probability that a molecule has a speed greater than some specified value.

Comprehension

7.2.1 Distinguish between the probability that a molecule has a velocity component greater than some specified value and the probability that the magnitude of the velocity component is greater than some value.

7.2.2 Identify and account for the differences in the shape of the probability density functions for the molecular speeds and energies at low values.

7.2.3 Describe the argument by which the flux of molecules normal to a surface can be determined.

7.2.4 Relate the pressure to the rate of momentum transfer resulting from molecular collisions with the walls of the container.

7.2.5 Describe the argument by which the pressure can be deduced from the Maxwell-Boltzmann velocity distribution.

Application

Calculate, given tables of the relevant integrals

7.3.1 the probability that a molecule has a velocity component greater than some value relative to $(2kT/m)^{1/2}$.

7.3.2 the probability that a molecule has a speed greater than some value relative to $(2kT/m)^{1/2}$.

7.3.3 the probability that a molecule has an energy greater than some value relative to kT.

Analysis

7.4.1 Express the probability that a molecule has a velocity component greater than some specified value in terms of the error function integral.

7.4.2 Express the probability that a molecule has a speed greater than some specified value in terms of the error function integral.

7.4.3 Derive the probability that a molecule has an energy greater than some specified value from the distribution of molecular speeds.

7.4.4 Justify the steps in the derivation of the expression for the flux of molecules normal to a surface, and in the kinetic derivation of the perfect gas equation of state.

Table of the Error Function, erf x.

x	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	0.00000	0.01128	0.02256	0.03384	0.04511	0.05637	0.06762	0.07886	0.09008	0.10128
0.1	0.11246	0.12362	0.13476	0.14587	0.15695	0.16800	0.17901	0.18999	0.20094	0.21184
0.2	0.22270	0.23352	0.24430	0.25502	0.26570	0.27633	0.28690	0.29742	0.30788	0.31828
0.3	0.32863	0.33891	0.34913	0.35928	0.36936	0.37938	0.38933	0.39921	0.40901	0.41874
0.4	0.42839	0.43797	0.44747	0.45689	0.46622	0.47548	0.48466	0.49374	0.50275	0.51167
0.5	0.52050	0.52924	0.53790	0.54646	0.55494	0.56332	0.57162	0.57982	0.58792	0.59594
0.6	0.60386	0.61168	0.61941	0.62705	0.63459	0.64203	0.64938	0.65663	0.66378	0.67084
0.7	0.67780	0.68467	0.69143	0.69810	0.70468	0.71116	0.71754	0.72382	0.73001	0.73610
0.8	0.74210	0.74800	0.75381	0.75952	0.76514	0.77067	0.77610	0.78144	0.78669	0.79184
0.9	0.79691	0.80188	0.80677	0.81156	0.81627	0.82089	0.82542	0.82987	0.83423	0.83851
1.0	0.84270	0.84681	0.85084	0.85478	0.85865	0.86244	0.86614	0.86977	0.87333	0.87680
1.1	0.88021	0.88353	0.88679	0.88997	0.89308	0.89612	0.89910	0.90200	0.90484	0.90761
1.2	0.91031	0.91296	0.91553	0.91805	0.92051	0.92290	0.92524	0.92751	0.92973	0.93190
1.3	0.93401	0.93606	0.93806	0.94001	0.94191	0.94376	0.94556	0.94731	0.94902	0.95067
1.4	0.95228	0.95385	0.95538	0.95686	0.95830	0.95969	0.96105	0.96237	0.96365	0.96490
1.5	0.96610	0.96728	0.96841	0.96952	0.97059	0.97162	0.97263	0.97360	0.97455	0.97546
1.6	0.97635	0.97721	0.97804	0.97884	0.97962	0.98038	0.98110	0.98181	0.98249	0.98315
1.7	0.98379	0.98441	0.98500	0.98558	0.98613	0.98667	0.98719	0.98769	0.98817	0.98864
1.8	0.98909	0.98952	0.98994	0.99035	0.99074	0.99111	0.99147	0.99182	0.99216	0.99248
1.9	0.99279	0.99309	0.99338	0.99366	0.99392	0.99418	0.99443	0.99466	0.99489	0.99511
2.0	0.99532	0.99553	0.99572	0.99591	0.99609	0.99626	0.99642	0.99658	0.99673	0.99688
2.1	0.99702	0.99716	0.99728	0.99741	0.99753	0.99764	0.99775	0.99785	0.99795	0.99805
2.2	0.99814	0.99822	0.99831	0.99839	0.99846	0.99854	0.99861	0.99867	0.99874	0.99880
2.3	0.99886	0.99891	0.99897	0.99902	0.99906	0.99911	0.99915	0.99920	0.99924	0.99927
2.4	0.99931	0.99935	0.99938	0.99941	0.99944	0.99947	0.99950	0.99952	0.99955	0.99957
2.5	0.99959	0.99961	0.99963	0.99965	0.99967	0.99969	0.99971	0.99972	0.99974	0.99975

Table of the gamma distribution function,

$$\frac{2}{\sqrt{\pi}}\int_0^x u^{1/2}e^{-u}\,du = 1 - \frac{2}{\sqrt{\pi}}\int_x^\infty u^{1/2}e^{-u}\,du$$

x	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	0.00075	0.00210	0.00384	0.00588	0.00816	0.01067	0.01336	0.01623	0.01925	0.02241
0.1	0.02570	0.02911	0.03263	0.03626	0.03997	0.04378	0.04766	0.05162	0.05566	0.05976
0.2	0.06392	0.06814	0.07241	0.07674	0.08111	0.08552	0.08998	0.09447	0.09900	0.10357
0.3	0.10816	0.11278	0.11743	0.12210	0.12680	0.13151	0.13624	0.14099	0.14576	0.15053
0.4	0.15532	0.16012	0.16493	0.16975	0.17457	0.17940	0.18423	0.18907	0.19391	0.19875
0.5	0.20359	0.20843	0.21326	0.21810	0.22293	0.22775	0.23257	0.23739	0.24219	0.24700
0.6	0.25179	0.25657	0.26135	0.26611	0.27087	0.27561	0.28034	0.28506	0.28977	0.29447
0.7	0.29915	0.30381	0.30847	0.31311	0.31773	0.32234	0.32693	0.33151	0.33607	0.34061
0.8	0.34514	0.34965	0.35414	0.35861	0.36307	0.36750	0.37192	0.37632	0.38070	0.38507
0.9	0.38941	0.39373	0.39803	0.40232	0.40658	0.41082	0.41505	0.41925	0.42343	0.42759
1.0	0.43173	0.43585	0.43995	0.44403	0.44809	0.45212	0.45614	0.46013	0.46410	0.46805
1.1	0.47198	0.47589	0.47977	0.48364	0.48748	0.49130	0.49510	0.49888	0.50263	0.50637
1.2	0.51008	0.51377	0.51744	0.52108	0.52471	0.52831	0.53189	0.53545	0.53899	0.54251
1.3	0.54601	0.54948	0.55293	0.55636	0.55977	0.56316	0.56653	0.56987	0.57320	0.57650
1.4	0.57978	0.58304	0.58628	0.58950	0.59270	0.59588	0.59903	0.60217	0.60528	0.60837
1.5	0.61145	0.61450	0.61753	0.62055	0.62354	0.62651	0.62946	0.63239	0.63530	0.63819
1.6	0.64107	0.64392	0.64675	0.64956	0.65236	0.65513	0.65789	0.66062	0.66334	0.66603
1.7	0.66871	0.67137	0.67401	0.67663	0.67924	0.68182	0.68439	0.68694	0.68947	0.69198
1.8	0.69447	0.69695	0.69940	0.70184	0.70427	0.70667	0.70906	0.71143	0.71378	0.71611
1.9	0.71843	0.72073	0.72302	0.72528	0.72753	0.72977	0.73198	0.73418	0.73637	0.73854
2.0	0.74069	0.74282	0.74494	0.74705	0.74913	0.75121	0.75326	0.75530	0.75733	0.75934
2.1	0.76133	0.76331	0.76528	0.76723	0.76916	0.77108	0.77299	0.77488	0.77675	0.77861
2.2	0.78046	0.78229	0.78411	0.78592	0.78771	0.78949	0.79125	0.79300	0.79474	0.79646
2.3	0.79817	0.79986	0.80154	0.80321	0.80487	0.80651	0.80814	0.80976	0.81137	0.81296
2.4	0.81454	0.81610	0.81766	0.81920	0.82073	0.82225	0.82376	0.82525	0.82673	0.82820
2.5	0.82966	0.83111	0.83254	0.83397	0.83538	0.83678	0.83817	0.83955	0.84092	0.84228

Problems

7.1 Find the probability that a molecule of mass m in a Maxwell-Boltzmann gas at temperature T has an x-component v_x of its velocity such that

(i) $v_x > (2kT/m)^{1/2}$

(ii) $v_x > 2(2kT/m)^{1/2}$

(iii) $(2kT/m)^{1/2} < v_x < 2(2kT/m)^{1/2}$

7.2 In a gas of nitrogen molecules (mass 4.648×10^{-26} kg) at 300 K, find the percentage with x-velocity components greater than 384.1 m/s.

7.3 What percentage of the gas molecules in Problem 7.2 have x-velocity components between -240.6 m/s and 240.6 m/s?

7.4 What percentage of the molecules in a Maxwell-Boltzmann gas have speeds

(i) greater than the most probable speed v_m?

(ii) greater than $2v_m$?

(iii) between v_m and $2v_m$?

7.5 Find the probability that a Maxwell-Boltzmann gas molecule will possess an energy

(i) less than $kT/2$

(ii) greater than kT

(iii) between $kT/2$ and kT.

7.6 The dependence of the rate of effusion on molecular mass was of great technical importance in providing a method of separating the isotopes of uranium in the form of uranium hexafluoride. Suppose we have a gas consisting of the molecules $^{238}U^{19}F_6$ and $^{235}U^{19}F_6$ in the natural isotopic abundances 99.3% and 0.7% respectively. Calculate the ratio of the fluxes of the two molecules through a small pinhole, and compare this with the ratio of concentrations in the original mixture.

Solutions

7.1(i) The required probability is obtained by use of equation 3:

$$P(v_x > v_0) = \frac{1}{2}\operatorname{erfc}(v_0\sqrt{\frac{m}{2kT}}) \qquad \text{where} \qquad v_0 = \sqrt{\frac{2kT}{m}}.$$

The argument of the complementary error function is clearly 1, so that

$$P(v_x > \sqrt{\frac{2kT}{m}}) = \frac{1}{2}\operatorname{erfc}(1) = 0.5 \times (1 - 0.84270)$$
$$= 0.07865.$$

(ii) Similarly we have

$$P(v_x > 2\sqrt{\frac{2kT}{m}}) = \frac{1}{2}\operatorname{erfc}(2) = 0.5 \times (1 - 0.99532)$$
$$= 0.00234.$$

(iii) These probabilities can be understood as areas under the curves showing the probability density for velocity components. We can therefore determine the probability that a molecule has a velocity component in the intermediate range as the difference between the probabilities (*i.e.*, areas) determined in parts (i) and (ii):

$$P(\sqrt{\frac{2kT}{m}} < v_x < 2\sqrt{\frac{2kT}{m}}) = P(v_x > \sqrt{\frac{2kT}{m}}) - P(v_x > 2\sqrt{\frac{2kT}{m}})$$
$$= 0.07865 - 0.00234 = 0.07631.$$

7.2 We first need to calculate the quantity

$$\sqrt{\frac{2kT}{m}} = \sqrt{\frac{2 \times (1.38066 \times 10^{-23}\ \mathrm{J\ K^{-1}}) \times (300\ \mathrm{K})}{(4.648 \times 10^{-26}\ \mathrm{kg})}} = 422.2\ \mathrm{m\ s^{-1}}.$$

The argument of the complementary error function is therefore

$$v_0\sqrt{\frac{m}{2kT}} = \frac{384.1}{422.2} = 0.90976 \simeq 0.91,$$

so that the required percentage is

$$P(v_0 > 384.1) \times 100\% = 100 \times \frac{1}{2}\operatorname{erfc}(0.91) = 100 \times 0.5 \times (1 - 0.80188)$$
$$= 9.9\%.$$

7.3 The probability that the x-velocity component is greater in magnitude than 240.6 m s^{-1} is given by equation (5), but the required probability is the complement of this, which is

$$P(|v_x| < v_0) = 1 - P(|v_x| > v_0) = \operatorname{erf}(v_0\sqrt{\frac{m}{2kT}}).$$

With $v_0 = 240.6$ m/s and the data of the previous problem, we have

$$P(|v_x| < 240.6 \text{ m s}^{-1}) = \text{erf}\,(\frac{240.6}{422.2}) = \text{erf}\,(0.57) = 0.57982,$$

so that 58% of the molecules have velocity components in the given range.

7.4 Solution of this problem requires application of equations 6 - 8:

$$P(v > v_0) = \frac{4}{\sqrt{\pi}}\int_{v_0/v_m}^{\infty} u^2\, e^{-u^2} du = \frac{2}{\sqrt{\pi}}(\frac{v_0}{v_m})\, e^{-(\frac{v_0}{v_m})^2} + \text{erfc}\,(\frac{v_0}{v_m}).$$

(i) We are given that $v_0 = v_m$, so that

$$P(v > v_m) = \frac{2}{\sqrt{\pi}} e^{-1} + \text{erfc}\,(1) = 0.41511 + 1 - 0.84270 = 0.57241.$$

This example illustrates the asymmetry of the distribution of molecular speeds as compared to that of the velocity components (the mean and most probable values are not the same).

(ii) With $v_0 = 2v_m$,

$$P(v > 2v_m) = \frac{4}{\sqrt{\pi}} e^{-4} + \text{erfc}(2)$$

$$= 0.04133 + 1 - 0.99532 = 0.04601.$$

(iii) From parts (i) and (ii),

$$P(v_m < v < 2v_m) = P(v > v_m) - P(v > 2v_m)$$

$$= 0.57421 - 0.04601 = 0.52820.$$

7.5 Applying equation (11),

$$P(E > E_0) = \frac{2}{\sqrt{\pi}}\int_{E_0/kT}^{\infty} u^{1/2} e^{-u} du = 1 - \frac{2}{\sqrt{\pi}}\int_{0}^{E_0/kT} u^{1/2} e^{-u} du.$$

(i) With $E_0 = kT/2$ we have

$$P(E < \frac{kT}{2}) = \frac{2}{\sqrt{\pi}}\int_{0}^{1/2} u^{1/2} e^{-u} du$$

$$= 0.20359.$$

(ii) With $E_0 = kT$,

$$P(E > kT) = \frac{2}{\sqrt{\pi}}\int_{1}^{\infty} u^{1/2} e^{-u} du = 1 - \frac{2}{\sqrt{\pi}}\int_{0}^{1} u^{1/2} e^{-u} du$$

$$= 1 - 0.43173 = 0.56827.$$

(iii) The fraction of molecules with energies in the intermediate range is determined by the condition that all three probabilities must sum to unity:

$$P(\frac{kT}{2} < E_0 < kT) = 1 - P(E_0 < \frac{kT}{2}) - P(E_0 > kT)$$

$$1 - 0.20359 - 0.56827 = 0.22814.$$

7.6 By application of equation 14, the ratio of the fluxes is

$$\frac{J_1}{J_2} = \frac{(N_1/V)}{(N_2/V)} \cdot \frac{<v_1>}{<v_2>}$$

$$= \frac{(N_1/V)}{(N_2/V)} \cdot \sqrt{\frac{m_2}{m_1}}.$$

If the subscript '1' refers to the molecule containing the lighter uranium isotope, the ratio of fluxes is

$$\frac{J_1}{J_2} = \frac{0.7}{99.3} \cdot \sqrt{\frac{352}{349}} = 7.08 \times 10^{-3},$$

while the ratio of concentrations in the original mixture is

$$\frac{(N_1/V)}{(N_2/V)} = \frac{0.7}{99.3} = 7.05 \times 10^{-3}.$$

Since the mass difference is so small, it is clear that the effusion process would have to be repeated many times to achieve an appreciable separation of the isotopes.

Statistical Thermodynamics Lecture No. 8

Our concern so far has been with the behaviour of perfect gases that are composed of atoms possessing only translational energy. In this lecture, we consider a perfect gas made up of diatomic molecules, and we construct a simple mechanical model to represent the behaviour of such molecules. The basic question of interest to us is how the rotation and vibration of the molecules contribute to the thermodynamic properties. If the atoms are treated as point masses m_a and m_b separated by a distance r_{ab}, the total energy of the molecule can be written as

$$\varepsilon = \frac{1}{2}m_a v_a^2 + \frac{1}{2}m_b v_b^2 + \Phi(r_{ab}) + \varepsilon_{pot} \tag{1}$$

where ε_{pot} is the potential energy due to external forces and $\Phi(r_{ab})$ is the potential energy of separation of the atoms. It is also possible to write the kinetic energy part of this expression in terms of the centre of mass. The position vector of the centre of mass is defined by

$$\mathbf{R} = \frac{m_a \mathbf{r}_a + m_b \mathbf{r}_b}{m_a + m_b} \tag{2}$$

and its velocity vector by

$$\mathbf{V} = \frac{m_a \mathbf{v}_a + m_b \mathbf{v}_b}{m_a + m_b}. \tag{3}$$

By use of simple algebra it is possible to express the sum of the kinetic energies of the individual atoms in terms of the translational kinetic energy of the molecule as a whole and an additional contribution to the kinetic energy associated with the relative motion of the atoms:

$$\frac{1}{2}m_a v_a^2 + \frac{1}{2}m_b v_b^2 = \frac{1}{2}(m_a + m_b)V^2 + \frac{1}{2}\frac{m_a m_b}{m_a + m_b}(\mathbf{v}_a - \mathbf{v}_b)^2. \tag{4}$$

If $\mathbf{r}_{ab}$ is the vector whose magnitude is the internuclear distance, the total molecular energy is

$$\varepsilon = \frac{1}{2}MV^2 + \frac{1}{2}\mu\left(\frac{d\mathbf{r}_{ab}}{dt}\right)^2 + \Phi(r_{ab}) + \varepsilon_{pot}. \tag{5}$$

where μ is the reduced mass. Both the magnitude and direction of this vector are time-dependent. We can identify a vibrational component of this time-dependence that can be written as

$$\left(\frac{d\mathbf{r}_{ab}}{dt}\right)_{vib} = \frac{\mathbf{r}_{ab}}{r_{ab}}\frac{dr_{ab}}{dt}. \tag{6}$$

Assuming that the internuclear separation is constant during the rotational motion, the rotational component is

$$\left(\frac{d\mathbf{r}_{ab}}{dt}\right)_{rot} = r_0(\omega_1 + \omega_2), \tag{7}$$

where ω_1 and ω_2 are angular velocities in two directions perpendicular to $\mathbf{r}_{ab}$.. For the total kinetic energy associated with changes in $\mathbf{r}_{ab}$ we therefore have

$$\frac{1}{2}\mu\left(\frac{d\mathbf{r}_{ab}}{dt}\right)^2 = \frac{1}{2}\mu\left(\frac{dr_{ab}}{dt}\right)^2 + \frac{1}{2}\mu r_0^2(\omega_1^2 + \omega_2^2). \tag{8}$$

where $\mu r_0^2/2$ is the moment of inertia, I. For nonlinear polyatomic molecules there are in general three moments of inertia and components of the angular velocity.

The potential energy of separation can be developed as a Taylor series about r_0:

$$\Phi(r) \simeq \Phi(r_0) + (r - r_0)\left(\frac{d\Phi}{dr}\right)_{r=r_0} + \frac{1}{2!}(r - r_0)^2\left(\frac{d^2\Phi}{dr^2}\right)_{r=r_0} + \dots$$

$$= -\varepsilon_0 + \frac{1}{2}\kappa(r - r_0)^2, \tag{9}$$

where higher terms in the expansion are neglected. In equation 9, ε_0 is the bond energy, and r_0 is assumed to be the *equilibrium bond length*, *i.e.*, the point at which the potential energy is a *minimum* (so that its first derivative with respect to r is zero). The potential energy curve is thus approximated by a parabola. The curvature κ of this parabola is known as the *force constant*, which is defined as

$$\kappa = \left(\frac{d^2\Phi}{dr^2}\right)_{r=r_0}. \tag{10}$$

The assumption that the higher terms in the expansion are negligible is equivalent to the assumption that the force required to stretch the bond from its equilibrium length is proportional to the degree of extension. This is called the *harmonic approximation*. The total energy of the molecule according to this classical model is therefore

$$\varepsilon = \frac{1}{2}MV^2 + \frac{1}{2}I(\omega_1^2 + \omega_2^2) + \frac{1}{2}\mu\left(\frac{dr_{ab}}{dt}\right)^2 + \frac{1}{2}\kappa(r - r_0)^2 - \varepsilon_0 + \varepsilon_{pot}. \tag{11}$$

The contributions of each of these parts of the energy to the thermodynamic properties can be determined by evaluating the corresponding contributions to the partition function. We observe that since the contributions to the energy are additive, the molecular partition function is formed as the product of the partition functions corresponding to each component of the molecular energy:

$$z = z_{trans}z_{rot}z_{vib}z_{pot}. \tag{12}$$

If we assume that the potential energy due to external forces acting on the molecules is zero, the contribution to the partition function is 1. The translational partition function is readily obtained as before by integrating over all possible values of the components of the centre-of-mass velocity:

$$z_{trans} = \frac{V}{h_0^3}\left(\frac{2\pi kT}{M}\right)^{3/2}. \tag{13}$$

To determine the rotational factor of the partition function, we have to integrate the Boltzmann factor for the kinetic energy over all values of the two angular velocity components:

$$z_{rot} = \frac{1}{(g_{0,r})^2}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp\left[-\frac{I\omega_1^2}{2kT} - \frac{I\omega_2^2}{2kT}\right] d\omega_1 d\omega_2$$

$$= \frac{1}{(g_{0,r})^2}\left(\int_{-\infty}^{\infty}\exp\left[-\frac{I\omega_1^2}{2kT}\right]d\omega_1\right)\left(\int_{-\infty}^{\infty}\exp\left[-\frac{I\omega_2}{2kT}\right]d\omega_2\right) = \frac{1}{(g_{0,r})^2}\frac{2\pi kT}{I}. \tag{14}$$

The quantity $g_{0,r}$ is inserted to ensure that the partition function is dimensionless, but for the purposes of the present discussion its actual value turns out to be immaterial.

To determine the vibrational factor, we have to integrate the Boltzmann factor for the kinetic and potential energies of vibration over all possible values of the separation and relative velocity of the atoms:

$$z_{vib} = \frac{1}{h_0}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\exp[-\frac{\kappa(r_{ab} - r_0)^2}{2kT} - \frac{\mu v_{ab}^2}{2kT}]dr_{ab}dv_{ab}$$

$$= \frac{1}{h_0}(\int_{-\infty}^{\infty}\exp[-\frac{\kappa r^2}{2kT}]dr)(\int_{-\infty}^{\infty}\exp[-\frac{\mu v_{ab}^2}{2kT}]dv_{ab}) = \frac{1}{h_0}\sqrt{\frac{2\pi kT}{\kappa}}\sqrt{\frac{2\pi kT}{\mu}}. \qquad (15)$$

The above analysis shows that each component of the molecular energy that depends on the square of some coordinate (*e.g.*, a linear or angular velocity, or degree of bond extension) the partition function will be proportional to the square root of kT. Generally, if the energy of a molecule is given by

$$\varepsilon = \varepsilon' + \alpha s^2 \qquad (16)$$

where s is an internal or external coordinate that can vary continuously over an infinite range, the partition function will always be of the form

$$z = z'\int_{-\infty}^{\infty}\exp(-\frac{\alpha s^2}{kT})\,ds = z'\sqrt{\frac{\pi kT}{\alpha}}. \qquad (17)$$

A further important observation is that each such component will contribute $kT/2$ to the average molecular energy (*i.e.*, to the internal energy per molecule), irrespective of the value of α. This result is known as the *Equipartition Theorem*, because the energy is distributed equally among all such quadratic degrees of freedom. Returning to our simple classical model for a diatomic molecule, we see that there are seven coordinates upon which the energy depends quadratically: three components of the centre-of-mass velocity, two angular velocity components, and the kinetic and potential energies of vibration. We therefore predict that the internal energy for a gas of N of these diatomic molecules is

$$U = N\frac{7kT}{2}, \quad \text{so that} \quad C_V = (\frac{\partial U}{\partial T})_V = \frac{7Nk}{2},$$

$$\text{and} \quad C_p = C_V + Nk = \frac{9Nk}{2}. \qquad (18)$$

In general, the motion of a molecule containing n atoms can be described by three velocity components and three angular velocity components (two for a linear molecule). The remaining $3n - 6$ (or $3n - 5$) coordinates required are associated with the *normal modes* of vibration. According to the Equipartition Theorem, each translational and rotational degree of freedom gives rise to $kT/2$ to the mean molecular energy, and each vibration contributes twice this amount. In the particular case where $n = 2$, the predictions of this simple model can be examined by determining the ratio of the heat capacities. The prediction is $\gamma = 9/7 \simeq 1.286$, but this value is found to be substantially different from the values for real gases. Data for some common diatomic molecules at 15°C and 1 atm are as follows:

Gas	$\gamma = C_p/C_V$
H_2	1.408
O_2	1.400
N_2	1.404
CO	1.404
Cl_2	1.34

This discrepancy could not be explained satisfactorily until the advent of the quantum theory of molecular vibration.

Learning Objectives

Knowledge

8.1.1 State defining formulae for centre of mass, reduced mass, and moment of inertia.

8.1.2 Identify potential and kinetic components of the energy of a diatomic molecule.

Comprehension

8.2.1 Describe the physical significance of the centre of mass.

8.2.2 Explain qualitatively the origin of rotational and vibrational components of the molecular velocity in terms of the time dependence of the internuclear separation vector.

8.2.3 Describe the physical significance of the harmonic approximation to the internuclear potential energy function.

8.2.4 Explain why additive contributions to the molecular energy produce multiplicative factors in the molecular partition function.

Application

8.3.1 Enumerate the mechanical degrees of freedom for a polyatomic molecule.

8.3.2 Assuming the validity of the Equipartition Theorem, estimate the internal energy and heat capacity ratio for an ideal polyatomic gas.

Analysis

8.4.1 Derive equation 4.

8.4.2 Demonstrate the equivalence of the parabolic potential energy curve and the linear relation between the force and degree of extension.

8.4.3 Demonstrate the constancy of the curvature for the parabolic potential energy curve.

8.4.4 Prove equation 17 by application of the formula for the Gaussian integral G_0.

8.4.5 Prove that each factor of the partition function corresponding to an energy depending quadratically on a coordinate contributes $kT/2$ to the internal energy.

Statistical Thermodynamics Lecture No. 9

We commenced our study of statistical thermodynamics by observing that although it is in principle possible to specify exactly the position and momentum of a particle by solving the equations of motion, the huge numbers of particles present in real systems compel us to adopt a statistical approach. Our treatment of the translational energy of molecules in perfect gases was based on the assumption that the molecular velocity and energy can be regarded as continuously variable, and resulted in predictions that are in good agreement with experiment, but in the last lecture, we showed that application of the same assumption to molecules possessing rotational and vibrational energies is not as successful. In this lecture, we show that the adoption of a quantum-mechanical treatment of vibration and rotation leads to much better agreement with experiment.

According to quantum mechanics, the behaviour of a particle of mass m can be determined in terms of *wave functions*, which are solutions of Schroedinger's equation:

$$\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E - U)\psi = 0, \qquad (1)$$

where E is the total energy (potential plus kinetic), U is the potential energy (as a function of position), and h is Planck's constant, and the first term on the left-hand side is the Laplacian of ψ (which is the sum of second partial derivatives of ψ with respect to the various coordinates). Two fundamental differences between the classical and quantum treatments can be identified. The first is that the position of the particle is not described in a deterministic way, but rather in terms of a probability density function that is obtained from the square of the wave function. The absolute limit to the accuracy with which we can describe the behaviour of a particle is expressed by the Heisenberg Uncertainty Principle

$$\Delta p.\Delta x \geq \frac{h}{4\pi}, \qquad (2)$$

where Δx and Δp are the uncertainties in position and momentum. The second difference is that the boundary conditions that must be satisfied by solutions of Schroedinger's equation make it possible for the energy E to assume only discrete values. From the point of view of statistical mechanics, this means that the partition functions will in general involve summations over these energy states rather than integration over continuous ranges of energy, but as we shall see, these sums can under some circumstances be accurately approximated by integrals.

The quantum-mechanical treatment of translation is based on a model called the 'particle in a box'. In this model, a particle of mass is m constrained to move within a rectangular region of space of volume $V = abc$, within which the potential energy is zero, and outside which the potential energy is infinite. The solution of the Schroedinger equation for this model leads to the result that the allowable (kinetic plus potential) energies are

$$E = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right), \qquad (3)$$

where n_1, n_2 and n_3 are the *quantum numbers* for motion in the x, y and z directions. The partition function is obtained by summing over all possible values of these quantum numbers:

$$z = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\sum_{n_3=0}^{\infty}\exp\left[-\frac{h^2}{8mkT}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)\right]. \qquad (4)$$

Because h^2 is so small, the energy levels corresponding to consecutive values of the ns are so closely spaced that the sums can be replaced, with negligible error, by integrals:

$$z \simeq \int_0^{\infty}\int_0^{\infty}\int_0^{\infty}\exp\left[-\frac{h^2}{8mkT}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)\right]dn_1 dn_2 dn_3$$

$$= \left(\int_0^\infty \exp[-\frac{n_1^2h^2}{8ma^2kT}]dn_1\right)\left(\int_0^\infty \exp[-\frac{n_2^2h^2}{8mb^2kT}]dn_2\right)\left(\int_0^\infty \exp[-\frac{n_3^2h^2}{8mc^2kT}]dn_3\right)$$

$$= \frac{(2\pi mkT)^{3/2}}{h^3}V. \qquad (5)$$

The internal energy is therefore

$$U = NkT^2\left(\frac{\partial \ln z}{\partial T}\right)_V = \frac{3NkT}{2}, \qquad (6)$$

which is seen to be exactly the same as that predicted by the Equipartition Theorem ($3kT/2$ per translational degree of freedom). We also see that the partition function becomes equal to that predicted by the classical model if we set

$$h_0 = \frac{h}{m}. \qquad (7)$$

But from equation 2, this quantity (apart from a trivial factor of 4π) represents the minimum value of the product of the uncertainties in position and velocity. Thus, from the point of view of statistical mechanics, the significance of the Uncertainty Principle is that it defines the smallest possible volume element of phase space in which we can say that a particle is located. In other words, we must regard the position-momentum phase space for a single particle as a collection of cells with a volume h, rather than as being completely continuous.

Solution of the Schroedinger equation for a rotating diatomic molecule leads to the result that the allowable energy levels are given by

$$E_{rot} = BJ(J+1), \qquad \text{where} \qquad B = \frac{h^2}{8\pi^2 I} \qquad (8)$$

where B is the rotational constant, I is the (single) moment of inertia and $J = 0,1,2,...$ is the rotational quantum number. (The rotational constant defined in equation 8 is expressed in J, and should be distinguished from the quantity determined from spectroscopy, which is usually expressed in wavenumber units. The spectroscopic rotational constant must be multiplied by hc to convert it to J). A further important point is that there are $2J + 1$ quantum states of the same energy for each value of J (*i.e.* the degeneracy is equal to $2J + 1$); this degeneracy can be removed by application of a strong electric field (the Stark effect from microwave spectroscopy). We must also take account of the fact that for symmetrical molecules, rotation produces nuclear configurations that are apparently indistinguishable. The corresponding partition function can therefore be written

$$z_{rot} = \frac{1}{\sigma}\sum_{J=0}^{\infty}(2J+1)\exp[-\frac{BJ(J+1)}{kT}], \qquad (9)$$

where σ is the symmetry number, which is either 1 (for a heteronuclear) or two (for a homonuclear) diatomic molecule. For sufficiently high temperatures, or for molecules with very small values of B (*i.e.*, large moments of inertia), this sum can also be approximated by an integral that can be conveniently evaluated by observing that the derivative of $J(J + 1)$ with respect to J is $2J + 1$:

$$z_{rot} \simeq \frac{1}{\sigma}\int_0^\infty (2J+1)\exp[-\frac{B}{kT}J(J+1)]dJ = \frac{kT}{\sigma B}. \qquad (10)$$

The rotational contribution to the internal energy is again seen to be in agreement with that obtained from the Equipartition Theorem, since it is formally equivalent to the contribution of two factors of $kT/2$ to the internal energy.

The simple harmonic oscillator model introduced in the last lecture can also be treated quantum-mechanically. This analysis leads to the result that the allowed vibrational energies are

$$E_{vib} = (v + \frac{1}{2})h\nu, \tag{11}$$

where ν is the vibrational frequency and v is the vibrational quantum number. The vibrational partition function is

$$z_{vib} = \sum_{v=0}^{\infty} \exp[-\frac{(v + \frac{1}{2})h\nu}{kT}] = \exp(-\frac{h\nu}{2kT})\sum_{v=0}^{\infty} \exp(-\frac{h\nu}{kT})^{v}$$

$$= \frac{\exp(-\frac{h\nu}{2kT})}{1 - \exp(-\frac{h\nu}{kT})}, \tag{12}$$

where the last step follows from the formula for the sum of a geometrical series. The internal energy of a gas of N particles is therefore

$$U_{vib} = NkT^2(\frac{\partial \ln z_{vib}}{\partial T})_V = \frac{Nh\nu}{2} + \frac{Nh\nu}{\exp(\frac{h\nu}{kT}) - 1}. \tag{13}$$

This looks very different from what we would expect from the kT per molecule that results from the Equipartition Theorem, because of both the presence of the exponential function and the constant term $Nh\nu/2$. The classical and quantum treatments agree only in the limit of high temperatures, where the exponential in the denominator of the last term in equation 13 can be approximated by its linear expansion:

$$\frac{Nh\nu}{\exp(\frac{h\nu}{kT}) - 1} \simeq \frac{Nh\nu}{1 + \frac{h\nu}{kT} - 1} = NkT. \tag{14}$$

As an example, consider the HCl molecule, for which the vibrational frequency is 8.65×10^{13} Hz. At 300 K, we have

$$\frac{h\nu}{kT} = \frac{(6.63 \times 10^{-34}\ \mathrm{J\ s}) \times (8.65 \times 10^{13}\ \mathrm{s}^{-1})}{(1.38 \times 10^{-23}\ \mathrm{J\ K}^{-1}) \times (300\ \mathrm{K})} = 13.8, \tag{15}$$

from which it follows that the ratio of the populations of the $v = 1$ and $v = 0$ states is

$$\frac{N_{v=1}}{N_{v=0}} = \exp(-\frac{h\nu}{kT}) = 1.02 \times 10^{-6}. \tag{16}$$

The spacing between the consecutive energy levels is equal to kT when

$$T = \frac{(6.63 \times 10^{-34}\ \mathrm{J\ s}) \times (8.65 \times 10^{13}\ \mathrm{s}^{-1})}{(1.38 \times 10^{-23}\ \mathrm{J\ K}^{-1})} = 4156\ \mathrm{K}, \tag{17}$$

from which it is clear that the molecule will disintegrate long before the approximation used in equation 14 is justified (the error in approximating $\exp x$ by $1 + x$ is about 0.5% if $x = 0.1$). It is also clear that the Equipartition Theorem overestimates the vibrational contribution to internal energy, since the vast majority of molecules are in the lowest vibrational state. Of course, the extent of this overestimation depends on the value of ν, which is a direct measure of the strength of a bond: the higher the frequency, the stronger the bond. For a weakly-bound molecule like iodine, for which $\nu = 6.40 \times 10^{12}$ Hz, $h\nu/k = 307$ K, so that at 300 K the ratio of populations corresponding to equation 15 is $\exp(-307/300) = 0.359$.

Learning Objectives

Knowledge

9.1.1 State the Heisenberg Uncertainty Principle.

9.1.2 State the expressions for the translational, rotational and vibrational energies as deduced from quantum-mechanics (equations 3, 8 and 11).

Comprehension

9.2.1 Describe the main differences between quantum-mechanical and classical-mechanical systems.

9.2.2 Distinguish between the indeterminacy implied in statistical-mechanical models and that inherent in quantum-mechanical models.

9.2.3 Relate the presence of h in the particle-in-a-box partition function to the Heisenberg Uncertainty Principle and the discreteness of phase space.

9.2.4 Identify the assumptions inherent in the calculation of the rotational partition function according to equation 10.

Application

Calculate, for a diatomic molecule

9.3.1 the quantum-mechanical translational partition function.

9.3.2 the rotational partition function from equation 10, given the value of B determined, *e.g.*, from microwave spectroscopy.

9.3.3 the vibrational partition function from a vibrational frequency.

9.3.4 the populations of rotational and vibrational quantum states.

Analysis

9.4.1 Demonstrate the equality of the internal energy determined from the quantum-mechanical and classical partition functions for rotation and translation.

9.4.2 Derive equations 5, 10 and 12.

Statistical Thermodynamics Lecture No. 10

We saw in the last lecture how statistical mechanics can be applied when the motion of molecules is treated quantum-mechanically, and in particular how the quantum treatment of molecular vibration allows us to account for the failure of the Equipartition Theorem. In this lecture we first consider first some characteristics of the quantum theory of molecular translation that lead to a different perspective on the physical significance of the partition function. We then proceed to discuss some of the more practical aspects of how partition functions and the associated average energy contributions can be calculated for the rotational and vibrational degrees of freedom.

The translational partition function for a quantum gas was shown to be proportional to the volume of the container. We can rewrite this in a rather more compact way as follows:

$$z_{trans} = \frac{(2\pi mkT)^{3/2}}{h^3}V = \frac{V}{\Lambda^3}, \qquad (1)$$

where

$$\Lambda \equiv \frac{h}{\sqrt{2\pi mkT}}$$

is known as the *thermal De Broglie wavelength* of the particle. It is clear not only that this wavelength decreases with increasing temperature, so that the partition function increases, but that the translational contribution to the thermodynamic properties of the gas depends on the size of the container in relation to the cube of the thermal wavelength. Since the mass of a typical molecule is of the order of 10-26 kg, a corresponding order of magnitude estimate for Λ at 300 K is

$$\Lambda = \frac{h}{\sqrt{2\pi mkT}} = \frac{(6.63\times 10^{-34}\ \mathrm{J\ s})}{\sqrt{2\pi\times(10^{-26}\ \mathrm{kg})\times(1.38\times 10^{-23}\ \mathrm{J\ K^{-1}})\times(300\ \mathrm{K})}} = 41\ \mathrm{pm},$$

which is seen to be considerably smaller than the molecule itself. When the partition function is determined according to equation 1, enormous numbers are obtained.

We can give a physical interpretation of this behaviour of the translational partition function by observing that increasing the volume occupied by a gas increases the number of accessible microstates in two ways. We are obviously providing many more possible *spatial* arrangements of the molecules. From the expression for the particle-in-a-box energy levels, *viz.*

$$E = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right), \qquad (2)$$

it is also clear that when the dimensions a, b and c of the box are increased from atomic to macroscopic values (from 0.1 nm to, say, 0.1 m) the spacing between energy levels corresponding to consecutive values of the quantum numbers greatly decreases. Thus, we are also increasing the number of accessible *momentum* states. For example, consider a gas confined in a cavity of diameter 1 nm (which one might find in a gas-liquid dispersion or microporous solid). The separation between the energy levels is of the order of

$$\frac{(6.63\times 10^{-34}\ \mathrm{J\ s})^2}{8\times(10^{-26}\ \mathrm{kg})\times(10^{-9}\mathrm{m})^2} = 5.49\times 10^{-24}\ \mathrm{J} = 1.33\times 10^{-3}\ kT \text{ at } 300\ \mathrm{K}.$$

When the dimension of the container is increased to 0.1 m, this characteristic energy is decreased by a factor of 10^{16}, becoming so minute with respect to kT as to be truly negligible, so that the approximation of the partition function by an integral is completely justified. This example shows that the numerical value of a partition function is a quantitative measure of the volume of phase space accessible to a particle in the system.

The thermodynamic properties of the gas as a whole are determined by considering the range of accessible configurations in relation to the number of particles in the system. In gases under usual temperatures and pressures (~ 300 K and 1 atm), the number of accessible quantum states is very large relative to the number of particles. Under these conditions, the probability that the same quantum state is occupied by *more* than one molecule is completely negligible: we refer to such a gas as being in the *nondegenerate* limit. An important example of a system for which degeneracy effects are important is liquid helium, which possesses many fascinating and unusual properties. These are, however, beyond the scope of this course.

Similar observations on the physical significance of the partition function also apply to the rotational degrees of freedom. As we have seen, the position of a diatomic molecule in the rotational phase space is specified by the quantum number J, with each quantum state having a degeneracy of $2J + 1$. The partition function in the high-temperature limit is given by

$$z_{rot} = \frac{kT}{\sigma B} = \frac{T}{\Theta_{rot}}, \qquad \text{where} \qquad \Theta_{rot} = \frac{\sigma B}{k} \tag{3}$$

is the characteristic *rotational temperature* which, from the definition of rotational constant B, is inversely proportional to the moment of inertia of the molecule. A bond length of about 100 pm and molecular mass of about 10^{-26} kg produce a moment of inertia of the order of 10^{-46} kg m^2, which gives a typical rotational temperature of

$$\Theta_{rot} = \frac{B}{k} = \frac{(6.63 \times 10^{-34}\ \text{J s})^2}{8\pi^2 \times (10^{-46}\ \text{kg m}^2) \times (1.38 \times 10^{-23}\text{J K}^{-1})} = 4\ \text{K},$$

assuming that $\sigma = 1$. The partition function is seen to increase with increasing temperature, again indicating increased accessibility of the quantum states, but we must remember that the accuracy of the integration used to obtain equation 3 also depends on the value of T/Θ_{rot}. This limitation of accuracy is likely to be important for the hydrogen molecule, which is exceptionally light. By application of a result known as the Euler-Maclaurin Summation Formula, it is possible to derive a more accurate expression for the partition function sum that has the integral as a first approximation:

$$\sum_{J=0}^{\infty}(2J + 1)\exp[-xJ(J + 1)] = \frac{1}{x} + \frac{1}{2} + \frac{x - 2}{12} + \frac{x^2 - 3x}{720} + \ldots, \quad x = \frac{\Theta_{rot}}{T}. \tag{4}$$

For small values of x (less than about 0.01), the sum converges very slowly, but the accuracy of the approximation on the right-hand side is good. Values of the series for larger values of x can be readily determined by direct evaluation of the sum, and are tabulated in an Appendix. As an example of the use of these results, let us calculate the rotational partition function for the hydrogen fluoride molecule at 301.5 K, given that the rotational constant is

$$\bar{B} = 20.9560\ \text{cm}^{-1},\ B = hc\bar{B} = (6.6256 \times 10^{-34}\ \text{J s}) \times (2.99793 \times 10^{8}\text{m s}^{-1})$$
$$\times (2095.60\ \text{m}^{-1}) = 4.1625 \times 10^{-22}\text{J},$$

so that

$$\Theta_{rot} = \frac{\sigma B}{k} = \frac{1 \times (4.1625 \times 10^{-22}\ \mathrm{J})}{(1.3806 \times 10^{-23}\ \mathrm{J\,K^{-1}})} = 30.15\ \mathrm{K}.$$

At the given temperature, we have $T/\Theta_{rot} = 0.1$, so we find from the table that $z_{rot} = 9.4317$. Use of the integral approximation for this molecule would give a value of exactly 10, which is about 6% too large. The probable fraction of molecules in each rotational energy level is

$$P_J = \frac{N_J}{N} = \frac{(2J+1)\exp(-\frac{\Theta_{rot}}{T}J(J+1))}{z_{rot}}. \tag{5}$$

The exponential factor obviously decreases with increasing J, but because this is multiplied by the degeneracy of $2J + 1$, we expect this probability to go through a maximum for some value of J. This gives a distribution of the form shown in Figure 1.

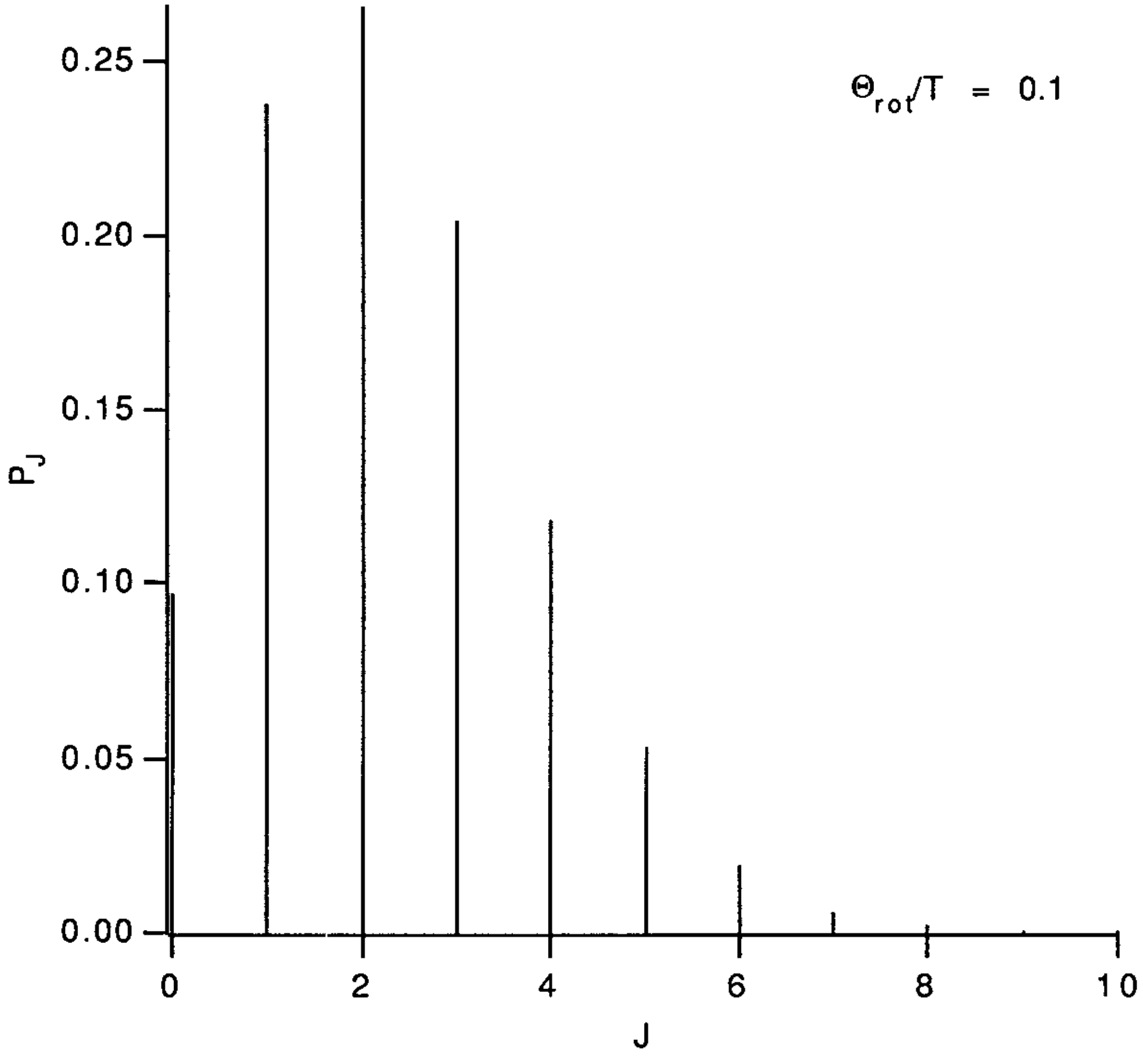


Figure 1: *Distribution among rotational energy states for HF at 301.5 K.*

The distribution of molecules among the vibrational energy states can also be conveniently expressed in terms of a characteristic temperature. For a molecule with a single vibration of frequency ν, the partition function is

$$z_{vib} = \sum_{v=0}^{\infty} \exp[-\frac{(v+\frac{1}{2})h\nu}{kT}] = \frac{\exp(-\frac{\Theta_{vib}}{2T})}{1 - \exp(-\frac{\Theta_{vib}}{T})}, \qquad (6)$$

where

$$\Theta_{vib} = \frac{h\nu}{k}.$$

Values of the vibrational temperatures are much higher than rotational temperatures: even for weakly-bound molecules, Θ_{vib} is several hundred K, and for most of the common diatomic molecules it is several thousand K. As a result, we can expect rather small values for the vibrational partition function factors. For example, the vibrational frequency of HF is 4139.04 cm^{-1}, so that

$$\nu = \bar{\nu}c = (413904\ m^{-1}) \times (2.99793 \times 10^{8}\ m\ s^{-1}) = 1.24086 \times 10^{14}\ s^{-1},$$

and

$$\Theta_{vib} = \frac{h\nu}{k} = \frac{(6.6256 \times 10^{-34}\ J\ s) \times (1.24086 \times 10^{14}\ s^{-1})}{(1.3806 \times 10^{-23}\ J\ K^{-1})} = 5955\ K.$$

At 301.5 K, the denominator of the vibrational partition function will be negligibly different from 1, and

$$z_{vib} \simeq \exp(-\frac{\Theta_{vib}}{2T}) = \exp(-\frac{5955}{2 \times 301.5}) = 4.894 \times 10^{-5}.$$

This small value corresponds to a very small volume of the vibrational phase space being available to the molecules at this temperature. In fact, the overwhelming majority of the molecules will be in the $v = 0$ state. The occupation probabilities of the higher vibrational states are as follows:

v	P_v
1	2.643×10^{-9}
2	6.987×10^{-18}
3	1.847×10^{-26}

Thus, only about 3 molecules per billion will be in the first excited state, about 7 per billion billion in the second excited state, and not even one molecule in a mole would be expected in the third state.

The calculations presented here have all been based on the assumption that the various components of the molecular energy are independent and additive, thus giving rise to factors of the partition function. This additivity assumption is known as the Born-Oppenheimer approximation, and is not strictly correct. In particular, there is appreciable interaction between rotational and vibrational degrees of freedom, resulting in a dependence of the rotational constant on the vibrational state. It should also be observed that the expressions for the energy levels are themselves approximations: the most accurate estimates of the thermodynamic properties can be derived from spectroscopically-determined energy levels.

Learning Objectives

Knowledge

10.1.1 Define the thermal wavelength of a quantum gas molecule.

Comprehension

10.2.1 Describe the behaviour of the thermal wavelength as a function of temperature.

10.2.2 Interpret the partition function as a measure of the accessible phase-space volume.

10.2.3 Describe the effect of changing the linear dimensions of the gas container on the configurations available to the gas molecules.

Application

Calculate

10.3.1 the thermal wavelength of a particle.

10.3.2 the rotational and vibrational temperatures of molecules from spectroscopic data.

10.3.3 the rotational and vibrational entropy and internal energy.

Analysis

10.4.1 Demonstrate the equivalence between characteristic temperature and separation between energy levels.

Rotational Partition Function

$$z_{rot} = \sum_{J=0}^{\infty}(2J+1)e^{-xJ(J+1)}, \qquad x = \frac{\Theta_{rot}}{T}.$$

x	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	100.3340	50.3347	33.6687	25.3360	20.3367	17.0040	14.6238	12.8387	11.4505
0.1	9.4317	8.6749	8.0345	7.4858	7.0103	6.5943	6.2274	5.9013	5.6096
0.2	5.1098	4.8941	4.6972	4.5168	4.3508	4.1977	4.0560	3.9245	3.8021
0.3	3.5811	3.4811	3.3871	3.2988	3.2155	3.1369	3.0626	2.9923	2.9256
0.4	2.8021	2.7448	2.6902	2.6382	2.5885	2.5410	2.4955	2.4520	2.4103
0.5	2.3319	2.2951	2.2596	2.2255	2.1927	2.1611	2.1306	2.1012	2.0729
0.6	2.0190	1.9935	1.9688	1.9448	1.9217	1.8993	1.8776	1.8565	1.8361
0.7	1.7972	1.7785	1.7604	1.7429	1.7258	1.7092	1.6931	1.6774	1.6622
0.8	1.6329	1.6188	1.6051	1.5918	1.5788	1.5661	1.5538	1.5418	1.5301
0.9	1.5075	1.4966	1.4860	1.4756	1.4655	1.4556	1.4460	1.4366	1.4274
1.0	1.4097	1.4011	1.3927	1.3846	1.3766	1.3688	1.3611	1.3537	1.3464
1.1	1.3322	1.3254	1.3187	1.3122	1.3058	1.2996	1.2935	1.2875	1.2816
1.2	1.2703	1.2648	1.2594	1.2542	1.2490	1.2440	1.2391	1.2342	1.2295
1.3	1.2203	1.2159	1.2116	1.2073	1.2031	1.1991	1.1951	1.1911	1.1873
1.4	1.1799	1.1763	1.1727	1.1693	1.1659	1.1626	1.1593	1.1562	1.1530

Statistical Thermodynamics Lecture No. 11

In our treatment so far we have been concerned with systems of weakly interacting particles, *i.e.*, those whose only interactions are through the kinetic energy exchanged in collisions. This level of treatment is quite adequate (and is indeed used) in the calculation of ideal-gas state thermodynamic quantities for gases from spectroscopic data: results of such calculations may be found in the JANAF Thermochemical Tables. On the other hand, the assumption of ideal-gas behaviour is obviously quite useless if we want to understand the volumetric properties of gases (as expressed by the equation of state).

To develop a theoretical model of imperfect gases, we first have to consider how we define the microstates of the system. In our work so far, we have characterised these microstates in terms of the coordinates of each molecule in a phase space consisting of the position and velocity coordinates. In a gas of interacting particles, the strength of the interactions obviously depends on the positions of the molecules with respect to each other. The thermodynamic functions are determined, in the usual way, by considering the contribution to the partition function of all possible values of the momentum of the particles and their positions with respect to each other. The way in which this can be done involves counting up the contributions of clusters of two, three,..., interacting molecules, averaging the Boltzmann factors of the energy of these clusters over all possible values of the separation distances and relative configurations.

The starting point in the analysis is the assumption that the total configurational energy of the gas can be written in the form

$$E = \sum_{i=1}^{N} \varepsilon_i + \sum_{i>j}^{N} \Phi(r_{ij}), \qquad (1)$$

where ε_i is the energy of molecule i arising from translation, internal degrees of freedom and external fields, and the summation of pairwise interaction potentials is over all *distinct* pairs (*e.g.*, pair 21 is counted but not 12). The partition function for the gas is obtained by integrating $\exp(-E/kT)$ over all accessible position and velocity coordinates of the molecules:

$$Z = Z_0 Z_{conf} \qquad (2)$$

where

$$Z_{conf} = \int \ldots \int \exp[-\frac{\sum_{i>j}^{N} \Phi(r_{ij})}{kT}] dr_1 \ldots dr_N.$$

and Z_0 is the partition function corresponding to the translational, rotational and vibrational degrees of freedom. We can't evaluate the integral in Z_{conf} in closed form but if the interaction potential energy is small with respect to kT, we can develop a series of approximations to it. To do this we observe that Boltzmann factor for the sum of the interaction energies can be written as a product of terms:

$$\exp[-\frac{\sum_{i>j}^{N} \Phi(r_{ij})}{kT}] = \prod_{i>j}^{N} \exp[-\frac{\Phi(r_{ij})}{kT}] = \prod_{i>j}^{N} [1 + f_{ij}], \qquad (3)$$

where

$$f_{ij} = \exp[-\frac{\Phi(r_{ij})}{kT}] - 1$$

is called a *Mayer f-function.* We observe that if the potential energy is small with respect to kT, the exponential will be close to 1 and the Mayer f-function much smaller than 1. The product of f-functions can be expanded as follows:

$$\prod_{i>j}^{N}[1+f_{ij}] = 1 + \sum_{i>j}^{N} f_{ij} + \text{other terms} \tag{4}$$

where the "other terms" involve sums of products of two, three,... f-functions, and correspond physically to interactions involving three, four,... molecules simultaneously. If the interactions are fairly weak, the f-functions are small, and we can regard the other terms as negligible and terminate the expansion after the second term. The configurational part of the partition function can therefore be approximated by

$$\begin{aligned} Z_{conf} &= \int\!....\!\int[1+\sum_{i>j}^{N} f_{ij}]d\mathbf{r}_1....d\mathbf{r}_N \\ &= V^N + \sum_{i>j}^{N}\int\!....\!\int f_{ij}d\mathbf{r}_1....d\mathbf{r}_N. \end{aligned} \tag{5}$$

We can evaluate each term in this sum by observing that each particular f-function depends only on the distance $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$, and is independent of the positions of all other molecules. (We also assume that the interaction potential between molecules i and j is spherically symmetric, *i.e.*, does not depend on the relative orientation of the molecules.) Integration with respect to each of the other $\mathbf{r}$s provides a factor of V, so that

$$\int\!....\!\int f_{ij}d\mathbf{r}_1....d\mathbf{r}_N = V^{N-2}\int\!\!\int f_{ij}(r_{ij})d\mathbf{r}_i d\mathbf{r}_j. \tag{6}$$

We can evaluate this integral either by specifying $\mathbf{r}_i$ and $\mathbf{r}_j$ separately with respect to some origin, or by specifying the position of one molecule ($\mathbf{r}_j$ say), and the position of the other molecule i $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$ with respect to it. Integrating over the positions of both molecules simultaneously is obviously equivalent to integrating over the position of one molecule and the relative position of the other, so we can write

$$d\mathbf{r}_i d\mathbf{r}_j = d\mathbf{r}_{ij} d\mathbf{r}_j \tag{7}$$

Integration over $\mathbf{r}_j$ produces another factor of V:

$$V^{N-2}\int\!\!\int f_{ij}(r_{ij})\, d\mathbf{r}_{ij} d\mathbf{r}_j = V^{N-1}\int f_{ij}(r_{ij})d\mathbf{r}_{ij}. \tag{8}$$

We now observe that this integral will have the same value for each of the $N(N-1)/2$ distinguishable pairs of indices i and j in the summation. Since for large N, $N(N-1)/2 \sim N^2/2$, the approximate partition function can be written in the form:

$$Z_{conf} \simeq V^N[1 - \frac{N^2 b(T)}{V}] \quad \text{where} \quad b(T) = \frac{1}{2}\int(1 - e^{-\frac{\Phi(r)}{kT}})d\mathbf{r}. \tag{9}$$

When transformed to polar coordinates, $d\mathbf{r} = 4\pi r^2 dr$, so that the integral b is

$$b(T) = 2\pi\int_0^\infty(1 - e^{-\frac{\Phi(r)}{kT}})r^2dr. \tag{10}$$

It is possible to show that a more accurate approximation is

$$Z_{conf} = V^N[1 - \frac{Nb(T)}{V}]^N. \tag{11}$$

The simplest justification of this expression is that the Helmholtz function $A = -kT \ln Z$ must be an extensive quantity, *i.e.*, the configurational factor of the partition function must be equal to the Nth power of some quantity. This condition is clearly satisfied by equation 11, and the square brackets in equation 9 can be recognised as the first two terms in the expansion. Equation 11 can be more rigorously justified by the observation that at low densities the dominant contribution to the expansion of products of f - functions comes from products where the factors contain no common indices. (For the details, which are intricate and rather tedious, see N. Davidson, 'Statistical Thermodynamics', New York: McGraw-Hill (1962)). The thermodynamic properties of the gas can be calculated from the total partition function

$$Z = Z_0 Z_{conf} = Z_0 V^N[1 - \frac{Nb(T)}{V}]^N. \tag{12}$$

In particular we are interested in the pressure:

$$p = kT\frac{\partial \ln Z}{\partial V} = kT\frac{\partial}{\partial V}[N \ln V + \ln Z_0 + N \ln (1 - \frac{Nb(T)}{V})]$$

$$\simeq kT\frac{\partial}{\partial V}[N \ln V + \ln Z_0 - \frac{N^2 b(T)}{V}], \tag{13}$$

where we have used the approximation $\ln(1 - Nb/V) \simeq -Nb/\mathrm{V}$, which is valid for low densities. We therefore obtain

$$p = \frac{NkT}{V} + (\frac{N}{V})^2 kT\, b(T) = \frac{NkT}{V}[1 + \frac{NkT}{V}] \tag{14}$$

The quantity $b(T)$ is of the order of the volume of a molecule. Introducing the number of moles, n, we obtain the two-term virial equation of state:

$$p = \frac{nRT}{V}[1 + \frac{n}{V}B(T)], \tag{15}$$

where B is the second virial coefficient defined by

$$B(T) = N_A b(T) = 2\pi N_A \int_0^\infty (1 - e^{-\frac{\Phi(r)}{kT}})r^2\, dr. \tag{16}$$

Equation 15 is widely used to calculate the thermodynamic properties of slightly imperfect gases, with emphasis on the word 'slightly': we should remember that the whole of the above analysis is based on the assumption that the 'other terms' in equation 4 are negligible. It is also worth remarking that we assumed that the potential is spherically symmetric (*i.e.*, does not allow for any dependence on the mutual orientations of the interacting molecules), which is likely to limit the applicability of equation 16 to atoms and almost spherical molecules; it is possible to generalise it to angle-dependent potentials but we do not pursue this refinement here. In general, numerical methods have to be used to evaluate the integral, but for some important simple interaction models, analytical results can be obtained.

The virial equation that we have obtained above is the simplest form of a more general equation of state that has the form of a power series in the number density N/V. The second, third,...coefficients in this expansion and correspond physically to contributions of interactions between groups of three, four,....molecules simultaneously. These coefficients can also be related in a general way to the pairwise potential energy of interaction, but they are exceedingly complicated, and difficult to evaluate even by computer.

Learning Objectives

Knowledge

11.1.1 State the equation for the total energy of a gas, including contributions from kinetic/internal degrees of freedom and interaction potential energy.

Comprehension

11.2.1 Describe how the microstates in an imperfect gas are characterised.

11.2.2 Describe how the assumption of pairwise additivity of intermolecular forces leads to equation 1.

11.2.3 Explain the origin of equation 3.

11.2.4 Identify the essential property of the Mayer *f*-functions and the assumptions that allow equation 4 to be obtained from equation 3.

11.2.5 Give a physical justification for the transformation of coordinates expressed by equation 7.

Application

11.3.1 Calculate the Mayer *f*-function, given the pairwise potential energy as a function of r.

Analysis

11.4.1 Justify equations 6, 8, 9, and 10.

11.4.2 Explain how equation 11 follows from equation 9 in terms of the properties of the Helmholtz function.

Statistical Thermodynamics Lecture No. 12

We showed in the last lecture how the assumptions that the total interaction potential energy in a real gas can be regarded as the sum of pairwise interactions, and that these interactions are small with respect to kT can be used to produce an expression for the second virial coefficient. Apart from its actual value, which obviously determines the magnitude of deviations from ideal-gas behaviour, the most important property of the second virial coefficient is its dependence on the temperature. In this lecture we consider the calculation of the second virial coefficient corresponding to various simple models of intermolecular interaction.

The simplest possible model for interactions is the hard-sphere model, which assumes that the potential energy of repulsion between molecules is either zero (if the molecules are not in contact) or infinite (if they are in contact) - see Figure 1. The crucial parameter in this model is the distance of closest approach r_s between the centres of the atoms or spherical molecules, which is obviously equal to twice the molecular radius. Corresponding values of the potential and the Mayer f-function for $r > r_s$ and $r < r_s$. are are follows:

$$\begin{array}{llll} r < r_s & \Phi = \infty & f(r) = \exp(-\frac{\Phi}{kT}) - 1 & = -1 \\ r > r_s & \Phi = 0 & f(r) & = 0 \end{array} \tag{1}$$

The second virial coefficient is therefore

$$\frac{B(T)}{N_A} = -2\pi\int_0^\infty f(r)r^2dr = 2\pi\int_0^{r_s} r^2dr = \frac{4\pi r_s^3}{3}, \tag{2}$$

which is seen to be equal to four times the molar volume, and temperature-independent. The fact that the virial coefficient is equal to four times the molecular volume rather than the molecular volume itself can readily be understood by considering the geometry of two spheres in contact, as shown in Figure 2. It is clear from this that the distance of closest approach defines a region of space around each molecule that cannot be occupied by other molecules. The volume of this spherical region is called the *excluded volume.*

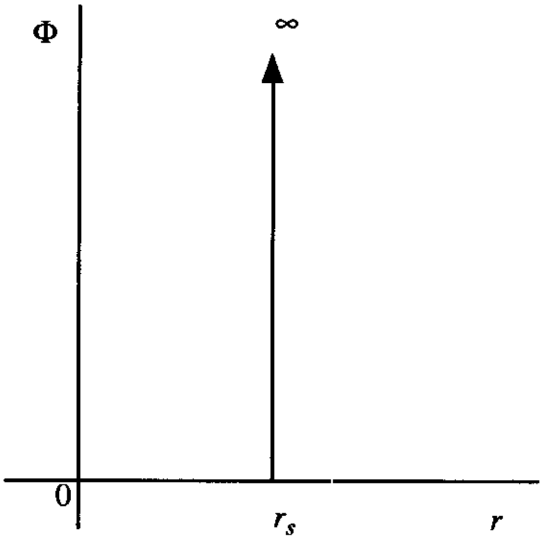


Figure 1: *Hard-Sphere Potential*

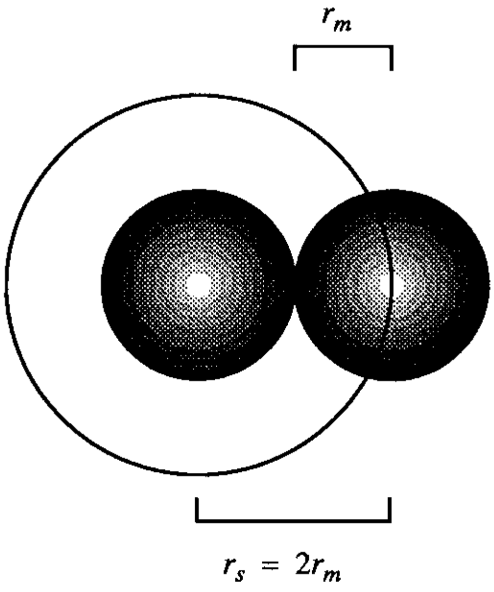


Figure 2: *Definition of the Excluded Volume*

In general, the *sign* of the virial coefficient can be related to the relative importance of attractive and repulsive regions of the potential function, and the behaviour of the f-function: if the potential energy is *positive* (as for a repulsive potential), f is *negative*, while if it is *negative* (attractive potential), f is *positive*. The temperature-independence of the virial coefficient according to the hard-sphere model is a major limitation to the usefulness of this particular model of interactions, since it is well known that the second virial coefficient depends quite strongly on temperature. A more realistic model that includes a constant attractive potential energy operating at intermediate distances as well as a distance of closest approach is the *square-well potential*. The corresponding values of the potential and the f-function for this model are:

$$\begin{array}{llll} r < r_s & \Phi = \infty & f(r) = \exp(-\frac{\Phi}{kT}) - 1 & = -1 \\ r_s < r < r_a & -\varepsilon & & \exp(\frac{\varepsilon}{kT}) - 1 \\ r > r_a & 0 & & 0 \end{array} \qquad (3)$$

so that the second virial coefficient is

$$\frac{B(T)}{N_A} = 2\pi \int_0^{r_s} r^2 dr - 2\pi(e^{\frac{\varepsilon}{kT}} - 1)\int_{r_s}^{r_a} r^2 dr$$

$$= \frac{16\pi r_m^3}{3} - \frac{16\pi}{3}(e^{\frac{\varepsilon}{kT}} - 1)(r_a^3 - r_m^3). \qquad (4)$$

The first term on the right-hand side is clearly the hard-sphere virial coefficient, to which B tends as the temperature increases (*i.e.*, as the exponential term becomes close to 1). The behaviour of this expression as a function of temperature can be visualised more clearly by considering the quantity

$$\frac{3B(T)}{16\pi r_m^3 N_A} = 1 - (e^{\frac{\varepsilon}{kT}} - 1)[(\frac{r_a}{r_m})^3 - 1] \qquad (5)$$

which is a reduced virial coefficient. This is shown as a function of ε/kT in Figure 3, and is seen to depend strongly on the cube of the ratio of the range of the potential and the molecular radius. This illustrates the physical significance of the virial coefficient as a measure of the volume around a molecule in which intermolecular forces are expected to be significant.

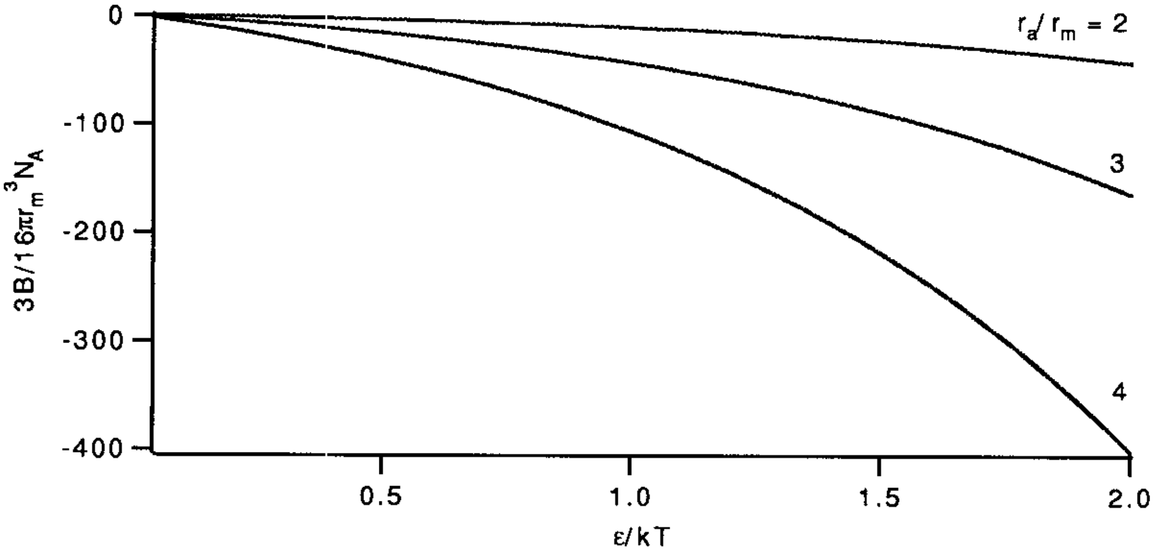


Figure 3: *Reduced virial coefficient for the square-well model.*

We observe that since the square-well model has three parameters, *viz.*, the molecular radius, the range of the attractive force and the depth of the potential well, we required several curves to represent the effect of all these parameters on the virial coefficient. For a two-parameter potential function, the same choice of dimensionless variables can be used for the independent and dependent variables, but only one curve is required - in other words, we can express the dimensionless second virial coefficient in terms of one parameter (the reduced energy ε/kT). The expression for this dimensionless virial coefficient can be derived for a general potential function that involves an energy parameter ε and a length parameter (usually the hard-sphere diameter) r_s, by defining the dimensionless quantities

$$R = \frac{r}{r_s} \qquad \Phi^* = \frac{\Phi}{\varepsilon} \qquad T^* = \frac{kT}{\varepsilon}. \tag{6}$$

We then have

$$B(T) = 2\pi N_A r_s^3 \int_0^\infty [1 - \exp(-\frac{\Phi^*\varepsilon}{kT})]R^2 dR \tag{7}$$

which can be written as

$$B^*(T^*) = \frac{3B(T)}{2\pi N_A r_s^3} = 3\int_0^\infty [1 - e^{-\frac{\Phi^*(R)}{T^*}}]R^2 dR, \tag{8}$$

where B^* is the second virial coefficient divided by the excluded volume per mole, v_0:

$$v_0 = \frac{2\pi N_A r_s^3}{3}. \tag{9}$$

Not only can the second virial coefficient be represented as a function of the single parameter T^*, but we can also see that all gases obey the same two-term viral equation of state:

$$p = \frac{RT}{v}[1 + \frac{B}{v}] = \frac{RT^*(\varepsilon/k)}{v^*v_0}[1 + \frac{B^*v_0}{v^*v_0}]$$

or

$$p^* = \frac{pv_0}{R\,(\varepsilon/k)} = \frac{T^*}{v^*}[1 + \frac{B^*}{v^*}]. \tag{10}$$

In our earlier discussion of the thermodynamics of nonideal gases, we found that for a two-parameter empirical cubic equation of state (such as the van der Waals equation), it was possible to relate the parameters to the critical constants of the gas and to show that all gases should obey the same equation of state in terms of the reduced state variables defined in terms of these critical constants. No assumptions about molecular interactions were required to obtain this result. The great significance of equation 10 is that it demonstrates that the principle of corresponding states also follows from the assumption of a two-parameter function to describe the pairwise potential energy of interaction as a function of intermolecular distance.

While this result is interesting in that it provides a common basis for comparing predictions of nonideal effects in different gases, we should not forget the rather drastic assumptions that were required in order to obtain the virial equation in the form used here. In particular, it is quite unrealistic to expect interactions between asymmetric molecules to be described satisfactorily by a spherically-symmetric two-parameter potential. Although as we mentioned earlier, it is possible to generalise the virial coefficient integral to deal with angle-dependent potentials, the currently-accepted interaction models are capable of accounting for the behaviour of only the simplest molecules.

The most successful and widely-used of the simple two-parameter potentials is that proposed by Lennard-Jones:

$$\Phi = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}], \tag{11}$$

where ε and σ are energy and distance parameters, respectively. The two terms in this expression predict a strong (but not infinitely strong) repulsive force that operates at short ranges, and an attractive force that varies more slowly with distance. (Physically, such an inverse sixth-power interaction is expected to arise from dispersion forces.) The reduced second virial coefficient for this model can be determined from equation 8 with $r_s = \sigma$,

$$B^*(T^*) = \frac{3B(T)}{2\pi N_A \sigma^3}, \qquad \text{and} \qquad T^* = \frac{kT}{\varepsilon}, \tag{12}$$

and can be shown to be

$$B^*(T^*) = -\sum_{j=0}^{\infty} \frac{2^{j+\frac{1}{2}}}{4j!} \Gamma(\frac{2j-1}{4}) \frac{1}{T^{*(2j+1)/4}}, \tag{13}$$

where Γ is the gamma function:

$$\Gamma(x) = \int_0^{\infty} t^{x-1} e^{-t}\, dt..$$

This virial coefficient is tabulated in an Appendix as a function of T^*. From this table it is evident that the virial coefficient is negative at low temperatures, indicating the dominance of the attractive term under such conditions. At high temperatures, it is not only positive, but passes through a rather poorly-defined maximum. Values of the Lennard-Jones parameters have been determined for many gases by fitting the equation to the experimental variation of the virial coefficient with temperature. Some representative values are as follows (J.O. Hirschfelder, C.F. Curtiss, and R.F. Bird, "Molecular Theory of Gases and Liquids", New York: Wiley (1954), p. 165):

Gas	(ε/k)/K	σ/Å	v_0/cm^3 mol^{-1}
Ne	34.9	2.78	27.10
Ar	119.8	3.405	49.80
Kr	171	3.60	58.86
N_2	95.05	3.698	63.78
O_2	118	3.46	52.26
CH_4	148.2	3.817	70.16
CO_2	189	4.486	113.9

Another potential that has proved useful is the Sutherland potential, which combines a hard-sphere repulsive potential with an inverse-power attraction. Thus:

$$\begin{aligned} r &< \sigma \qquad \Phi = \infty \\ r &> \sigma \qquad \Phi = -\frac{c}{r^{\gamma}} = -\varepsilon\,(\frac{\sigma}{r})^{\gamma}, \qquad \text{where} \qquad \varepsilon = \frac{c}{\sigma^{\gamma}}, \end{aligned} \tag{14}$$

where c and γ are constants. The second form of the inverse-power potential allows this function to be identified as the limiting form of the Lennard-Jones function in which the exponent of 12 in the first (repulsive) term is replaced by infinity. The second virial coefficient according to this model is

$$B(T) = \frac{2\pi N_A \sigma^3}{3} - 2\pi N_A \int_{\sigma}^{\infty} [\exp(\frac{c}{r^{\gamma} kT}) - 1] r^2 dr \tag{15}$$

or in dimensionless form

$$B^*(T^*) = \frac{3B(T)}{2\pi N_A \sigma^3} = 1 - \int_{1}^{\infty} (e^{\frac{1}{R^{\gamma} T^*}} - 1) R^2 dR. \tag{16}$$

This integral can be readily evaluated by expanding the exponential in a power series and integrating term-by-term:

$$B^*(T^*) = 1 - 3\sum_{j=1}^{\infty} \frac{1}{j!(j\gamma - 3)T^{*j}}, \qquad \text{where} \qquad T^* = \frac{kT}{\varepsilon}. \tag{17}$$

The case where the exponent $\gamma = 6$ is of particular importance, since as observed above, this is expected to result from dispersion forces. The reduced virial coefficient for this case is also tabulated as a function of T^*. The Sutherland model is a member of a class of potential functions known as *hard-core potentials*, which are of interest in that they can be related to the van der Waals equation of state. To see how this might be done, we observe that the limiting form of the Mayer f-function when the interaction potential is much less than kT, *viz.*:

$$f = \exp(-\frac{\Phi}{kT}) - 1 \simeq -\frac{\Phi}{kT}, \tag{18}$$

gives rise to a corresponding approximation for B:

$$B(T) = \frac{2\pi N_A \sigma^3}{3} + \frac{2\pi N_A}{kT} \int_{\sigma}^{\infty} \Phi(r)\, r^2 dr. \tag{19}$$

The van der Waals equation of state

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \tag{20}$$

can be approximated by a two-term virial equation if the molar volume v is much less than b:

$$p \simeq \frac{RT}{v}[1 + \frac{b}{v}] - \frac{a}{v^2} = \frac{RT}{v}[1 + (b - \frac{a}{RT})\frac{1}{v}]. \tag{21}$$

The virial coefficient in this equation is identical to that given by equation 19 if we set

$$b = \frac{2\pi N_A \sigma^3}{3} \qquad \text{and} \qquad -\frac{a}{RT} = \frac{2\pi N_A}{kT} \int_{\sigma}^{\infty} \Phi(r)\, r^2 dr. \tag{22}$$

Transformation to the dimensionless variables $R = r/\sigma$ and $\Phi^* = \Phi/\varepsilon$ allows the expression for a to be reduced further to

$$\frac{a}{3b} = -N_A \varepsilon \int_{1}^{\infty} \Phi^*(R)\, R^2 dR. \tag{23}$$

Although this connexion between the virial equation and the van der Waals equation is interesting, it should be remembered that the two equations can be regarded as equivalent only in the limit of low densities. From the practical point of view, the great advantage of the van der Waals equation is that it is capable of predicting vapour-liquid equilibrium, while the two-term virial equation is not.

Learning Objectives

Knowledge

12.1.1 Describe the r-dependence of the hard-sphere, square-well, Lennard-Jones and Sutherland potentials.

Comprehension

12.2.1 Describe qualitatively the behaviour of the Mayer f-function according to the above potential models.

12.2.2 Relate the sign of the virial coefficient to the behaviour of the for potentials that are completely repulsive or completely attractive.

12.2.3 Describe qualitatively the variation of the reduced second virial coefficient as a function of reduced temperature, for each of the potential models.

Application

12.3.1 Calculate values of the Mayer f-function as a function of distance for a potential function given in either dimensioned or dimensionless form.

12.3.2 Determine second virial coefficients of actual gases from the tabulations of reduced virial coefficients and the values of the relevant parameters.

Analysis

12.4.1 Demonstrate the relation between the excluded volume and molecular volume for the hard-sphere model.

12.4.2 Derive the expression for the reduced second virial coefficient according to a two-parameter potential function.

12.4.3 Derive the principle of corresponding states from the general form of the second virial coefficient for a two-parameter potential function.

12.4.4 Identify the approximations made in the identification of the van der Waals parameters in terms of the virial coefficient for a hard-core potential function.

Reduced Second Virial Coefficient for the Lennard-Jones 6-12 Potential

Calculated according to the analytical equation given by Hirschfelder *et al.*, *op. cit.*, p.163:

$$B^*(T^*) = \frac{B(T)}{v_0} = -\sum_{j=0}^{\infty} \frac{2^{j+\frac{1}{2}}}{4j!}\Gamma\left(\frac{2j-1}{4}\right)\frac{1}{T^{*(2j+1)/4}}, \qquad T^* = \frac{kT}{\varepsilon}.$$

B*(0.10)= -9800.129 B*(0.20)= -110.5778

T*	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
0.0				-27.8806	-13.7988	-8.7202	-6.1980	-4.7100	-3.7342	-3.0471
1.0	-2.5381	-2.1464	-1.8359	-1.5841	-1.3758	-1.2009	-1.0519	-0.9236	-0.8120	-0.7141
2.0	-0.6276	-0.5506	-0.4817	-0.4197	-0.3636	-0.3126	-0.2661	-0.2236	-0.1845	-0.1485
3.0	-0.1152	-0.0844	-0.0558	-0.0291	-0.0043	0.0190	0.0407	0.0611	0.0803	0.0984
4.0	0.1154	0.1315	0.1467	0.1611	0.1747	0.1876	0.1999	0.2116	0.2227	0.2333
5.0	0.2433	0.2530	0.2622	0.2709	0.2794	0.2874	0.2951	0.3025	0.3096	0.3164
6.0	0.3229	0.3292	0.3352	0.3410	0.3466	0.3520	0.3572	0.3621	0.3670	0.3716
7.0	0.3761	0.3804	0.3846	0.3886	0.3925	0.3963	0.4000	0.4035	0.4069	0.4102
8.0	0.4134	0.4165	0.4196	0.4225	0.4253	0.4280	0.4307	0.4333	0.4358	0.4382
9.0	0.4406	0.4429	0.4451	0.4473	0.4494	0.4514	0.4534	0.4554	0.4573	0.4591
10.0	0.4609	0.4626	0.4643	0.4659	0.4675	0.4691	0.4706	0.4721	0.4735	0.4749
11.0	0.4763	0.4776	0.4789	0.4802	0.4814	0.4826	0.4838	0.4850	0.4861	0.4872
12.0	0.4882	0.4893	0.4903	0.4913	0.4922	0.4932	0.4941	0.4950	0.4958	0.4967
13.0	0.4975	0.4983	0.4991	0.4999	0.5007	0.5014	0.5021	0.5028	0.5035	0.5042
14.0	0.5048	0.5055	0.5061	0.5067	0.5073	0.5079	0.5084	0.5090	0.5095	0.5101
15.0	0.5106	0.5111	0.5116	0.5121	0.5125	0.5130	0.5134	0.5139	0.5143	0.5147
16.0	0.5151	0.5155	0.5159	0.5163	0.5167	0.5170	0.5174	0.5177	0.5181	0.5184
17.0	0.5187	0.5190	0.5193	0.5196	0.5199	0.5202	0.5205	0.5208	0.5210	0.5213
18.0	0.5215	0.5218	0.5220	0.5222	0.5225	0.5227	0.5229	0.5231	0.5233	0.5235
19.0	0.5237	0.5239	0.5241	0.5243	0.5244	0.5246	0.5248	0.5249	0.5251	0.5252
20.0	0.5254	0.5255	0.5257	0.5258	0.5259	0.5260	0.5262	0.5263	0.5264	0.5265
21.0	0.5266	0.5267	0.5268	0.5269	0.5270	0.5271	0.5272	0.5273	0.5273	0.5274
22.0	0.5275	0.5276	0.5276	0.5277	0.5277	0.5278	0.5279	0.5279	0.5280	0.5280
23.0	0.5281	0.5281	0.5281	0.5282	0.5282	0.5283	0.5283	0.5283	0.5283	0.5284
24.0	0.5284	0.5284	0.5284	0.5285	0.5285	0.5285	0.5285	0.5285	0.5285	0.5285
25.0	0.5285	0.5285	0.5285	0.5285	0.5285	0.5285	0.5285	0.5285	0.5285	0.5285
26.0	0.5285	0.5284	0.5284	0.5284	0.5284	0.5284	0.5284	0.5283	0.5283	0.5283
27.0	0.5283	0.5282	0.5282	0.5282	0.5281	0.5281	0.5281	0.5280	0.5280	0.5280
28.0	0.5279	0.5279	0.5278	0.5278	0.5277	0.5277	0.5277	0.5276	0.5276	0.5275
29.0	0.5275	0.5274	0.5274	0.5273	0.5273	0.5272	0.5272	0.5271	0.5270	0.5270
30.0	0.5269	0.5269	0.5268	0.5267	0.5267	0.5266	0.5266	0.5265	0.5264	0.5264

T*	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
30.	0.5269	0.5263	0.5256	0.5249	0.5241	0.5232	0.5223	0.5214	0.5205	0.5195
40.	0.5186	0.5176	0.5166	0.5156	0.5146	0.5135	0.5125	0.5115	0.5104	0.5094
50.	0.5084	0.5073	0.5063	0.5053	0.5042	0.5032	0.5022	0.5012	0.5002	0.4992
60.	0.4982	0.4972	0.4962	0.4953	0.4943	0.4933	0.4924	0.4914	0.4905	0.4896
70.	0.4887	0.4877	0.4868	0.4859	0.4850	0.4841	0.4832	0.4824	0.4815	0.4806
80.	0.4798	0.4789	0.4781	0.4773	0.4764	0.4756	0.4748	0.4740	0.4732	0.4724
90.	0.4716	0.4708	0.4701	0.4693	0.4685	0.4678	0.4670	0.4663	0.4655	0.4648
100.	0.4641	0.4633	0.4626	0.4619	0.4612	0.4605	0.4598	0.4591	0.4584	0.4578

T*	0.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0
100.	0.4641	0.4571	0.4506	0.4446	0.4389	0.4337	0.4287	0.4240	0.4196	0.4154
200.	0.4114	0.4076	0.4040	0.4006	0.3973	0.3942	0.3911	0.3882	0.3854	0.3827
300.	0.3801	0.3776	0.3752	0.3729	0.3706	0.3684	0.3663	0.3642	0.3622	0.3602
400.	0.3584	0.3565	0.3547	0.3530	0.3513	0.3496	0.3480	0.3464	0.3449	0.3433
500.	0.3419	0.3404	0.3390	0.3376	0.3363	0.3350	0.3337	0.3324	0.3311	0.3299
600.	0.3287	0.3275	0.3264	0.3252	0.3241	0.3230	0.3220	0.3209	0.3199	0.3188
700.	0.3178	0.3168	0.3159	0.3149	0.3140	0.3130	0.3121	0.3112	0.3103	0.3095
800.	0.3086	0.3078	0.3069	0.3061	0.3053	0.3045	0.3037	0.3029	0.3021	0.3014
900.	0.3006	0.2999	0.2991	0.2984	0.2977	0.2970	0.2963	0.2956	0.2949	0.2943

Reduced Second Virial Coefficient for the Sutherland Potential (Exponent 6)

$$B^*(T^*) = \frac{B(T)}{v_0} = 1 - 3\sum_{j=1}^{\infty}\frac{1}{j!(6j-3)T^{*j}}, \qquad T^* = \frac{kT}{\varepsilon}.$$

B*(0.10)= -1338.143

T*	0.00	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.90
0.0			-23.3084	-6.8154	-3.4289	-2.0688	-1.3452	-0.8975	-0.5934	-0.3735
1.0	-0.2070	-0.0766	0.0283	0.1146	0.1868	0.2481	0.3008	0.3465	0.3867	0.4222
2.0	0.4538	0.4821	0.5076	0.5307	0.5518	0.5710	0.5887	0.6050	0.6200	0.6339
3.0	0.6468	0.6589	0.6701	0.6807	0.6906	0.6999	0.7086	0.7169	0.7247	0.7320
4.0	0.7390	0.7457	0.7520	0.7580	0.7637	0.7692	0.7744	0.7794	0.7841	0.7887
5.0	0.7931	0.7973	0.8013	0.8052	0.8089	0.8125	0.8159	0.8192	0.8225	0.8256
6.0	0.8285	0.8314	0.8342	0.8369	0.8396	0.8421	0.8445	0.8469	0.8492	0.8515
7.0	0.8536	0.8558	0.8578	0.8598	0.8617	0.8636	0.8655	0.8672	0.8690	0.8707
8.0	0.8723	0.8739	0.8755	0.8770	0.8785	0.8800	0.8814	0.8828	0.8842	0.8855
9.0	0.8868	0.8881	0.8893	0.8905	0.8917	0.8929	0.8940	0.8951	0.8962	0.8973
10.0	0.8983	0.8993	0.9003	0.9013	0.9023	0.9032	0.9041	0.9051	0.9060	0.9068
11.0	0.9077	0.9085	0.9094	0.9102	0.9110	0.9118	0.9125	0.9133	0.9140	0.9148
12.0	0.9155	0.9162	0.9169	0.9176	0.9183	0.9189	0.9196	0.9202	0.9208	0.9215
13.0	0.9221	0.9227	0.9233	0.9239	0.9244	0.9250	0.9256	0.9261	0.9266	0.9272
14.0	0.9277	0.9282	0.9287	0.9292	0.9297	0.9302	0.9307	0.9312	0.9317	0.9321
15.0	0.9326	0.9330	0.9335	0.9339	0.9344	0.9348	0.9352	0.9356	0.9360	0.9364
16.0	0.9368	0.9372	0.9376	0.9380	0.9384	0.9388	0.9391	0.9395	0.9399	0.9402
17.0	0.9406	0.9409	0.9413	0.9416	0.9420	0.9423	0.9426	0.9430	0.9433	0.9436
18.0	0.9439	0.9442	0.9445	0.9449	0.9452	0.9455	0.9457	0.9460	0.9463	0.9466
19.0	0.9469	0.9472	0.9475	0.9477	0.9480	0.9483	0.9485	0.9488	0.9491	0.9493
20.0	0.9496	0.9498	0.9501	0.9503	0.9506	0.9508	0.9511	0.9513	0.9515	0.9518
21.0	0.9520	0.9522	0.9525	0.9527	0.9529	0.9531	0.9533	0.9536	0.9538	0.9540
22.0	0.9542	0.9544	0.9546	0.9548	0.9550	0.9552	0.9554	0.9556	0.9558	0.9560
23.0	0.9562	0.9564	0.9566	0.9568	0.9570	0.9571	0.9573	0.9575	0.9577	0.9579
24.0	0.9580	0.9582	0.9584	0.9586	0.9587	0.9589	0.9591	0.9592	0.9594	0.9596
25.0	0.9597	0.9599	0.9601	0.9602	0.9604	0.9605	0.9607	0.9608	0.9610	0.9611
26.0	0.9613	0.9614	0.9616	0.9617	0.9619	0.9620	0.9622	0.9623	0.9625	0.9626
27.0	0.9627	0.9629	0.9630	0.9631	0.9633	0.9634	0.9635	0.9637	0.9638	0.9639
28.0	0.9641	0.9642	0.9643	0.9645	0.9646	0.9647	0.9648	0.9650	0.9651	0.9652
29.0	0.9653	0.9654	0.9656	0.9657	0.9658	0.9659	0.9660	0.9661	0.9663	0.9664
30.0	0.9665	0.9666	0.9667	0.9668	0.9669	0.9670	0.9671	0.9672	0.9674	0.9675

T*	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0
30.	0.9665	0.9676	0.9686	0.9695	0.9704	0.9713	0.9721	0.9729	0.9736	0.9742
40.	0.9749	0.9755	0.9761	0.9767	0.9772	0.9777	0.9782	0.9786	0.9791	0.9795
50.	0.9799	0.9803	0.9807	0.9811	0.9814	0.9818	0.9821	0.9824	0.9827	0.9830
60.	0.9833	0.9836	0.9838	0.9841	0.9843	0.9846	0.9848	0.9850	0.9853	0.9855
70.	0.9857	0.9859	0.9861	0.9863	0.9865	0.9866	0.9868	0.9870	0.9872	0.9873
80.	0.9875	0.9876	0.9878	0.9879	0.9881	0.9882	0.9883	0.9885	0.9886	0.9887
90.	0.9889	0.9890	0.9891	0.9892	0.9893	0.9895	0.9896	0.9897	0.9898	0.9899
100.	0.9900	0.9901	0.9902	0.9903	0.9904	0.9905	0.9906	0.9906	0.9907	0.9908

T*	0.0	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0
100.	0.9900	0.9909	0.9917	0.9923	0.9928	0.9933	0.9937	0.9941	0.9944	0.9947
200.	0.9950	0.9952	0.9955	0.9956	0.9958	0.9960	0.9962	0.9963	0.9964	0.9965
300.	0.9967	0.9968	0.9969	0.9970	0.9971	0.9971	0.9972	0.9973	0.9974	0.9974
400.	0.9975	0.9976	0.9976	0.9977	0.9977	0.9978	0.9978	0.9979	0.9979	0.9980
500.	0.9980	0.9980	0.9981	0.9981	0.9981	0.9982	0.9982	0.9982	0.9983	0.9983
600.	0.9983	0.9984	0.9984	0.9984	0.9984	0.9985	0.9985	0.9985	0.9985	0.9986
700.	0.9986	0.9986	0.9986	0.9986	0.9986	0.9987	0.9987	0.9987	0.9987	0.9987
800.	0.9987	0.9988	0.9988	0.9988	0.9988	0.9988	0.9988	0.9989	0.9989	0.9989
900.	0.9989	0.9989	0.9989	0.9989	0.9989	0.9989	0.9990	0.9990	0.9990	0.9990

Statistical Thermodynamics Examination

(a)

(i) For a statistical-mechanical system that can assume singly-degenerate discrete energy levels E_k, $k = 1,2,...$, show that the expressions for the average energy

$$U = \langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}$$

and

$$\langle E \rangle = \sum_{k=0}^{\infty} E_k \frac{e^{-\beta E_k}}{Z}$$

are equivalent, where the partition function is defined by

$$Z = \sum_{k=0}^{\infty} e^{-\beta E_k} \qquad \text{and} \qquad \beta = \frac{1}{kT}$$

(5)

(ii) Demonstrate the equivalence of the definitions

$$S = -k \sum_{k=0}^{\infty} \mathrm{P}(E_k) \ln \mathrm{P}(E_k) \qquad \text{and} \qquad S = k \ln Z + \frac{U}{T}$$

$$\text{where} \qquad \mathrm{P}(E_k) = \frac{e^{-\beta E_k}}{Z}$$

(5)

(b)

An hypothetical system of noninteracting particles can distribute themselves among three states with energies $-\varepsilon$, 0, and $+\varepsilon$. Assuming that $\beta\varepsilon = 1$, calculate:

(i) the particle partition function;
(ii) the probability of occupation for each of the three states;
(iii) the average energy per particle in units of $1/\beta = kT$;
(iv) the entropy in units of k.

How would you expect your answers to differ qualitatively if the value $\beta\varepsilon = 0.01$ were selected instead? (No calculations are required.)

(15)

(c)

(i) The Maxwell-Boltzmann distribution function for the speeds of molecules of mass m is

$$\eta(v) = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right)$$

Use this to estimate the probability that a methane molecule (molar mass 16.04 g/mol) has a speed in the range (500 ± 0.5) m/s (*i.e.*, between 499.5 and 500.5 m/s).

(5)

(ii) Elementary textbooks on general chemistry frequently confuse the mean speed and root-mean-square speed of molecules in a gas. State how the mean- and mean-square-speeds can be defined in terms of integrals involving the function $\eta(v)$, and evaluate these integrals by application of the Gaussian Integral formulae

$$G_3 = \int_0^\infty x^3\, e^{-\alpha x^2}\, dx = \frac{1}{2\alpha^2} \qquad \text{and} \qquad G_4 = \int_0^\infty x^4\, e^{-\alpha x^2}\, dx = \frac{3}{8}\frac{\sqrt{\pi}}{\alpha^{5/2}}$$

where $\alpha > 0$.

(10)

(d)

(i) According to the quantum theory, the translational energy levels available to a particle of mass m in a rectangular box of dimensions a, b, and c are

$$\varepsilon_{n_1 n_2 n_3} = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2} + \frac{n_2^2}{b^2} + \frac{n_3^2}{c^2}\right)$$

By use of the Gaussian Integral formula

$$G_0 = \int_0^\infty e^{-\alpha x^2}\, dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$$

show that the translational partition function for such a particle is

$$z_{\text{trans}} = \frac{(2\pi mkT)^{3/2}}{h^3} V, \qquad \text{where} \qquad V = abc.$$

(5)

(ii) In the classical and quantum-mechanical treatments of the distribution of translational energies in a perfect gas, the linear dimensions of the container appear in the partition function as the product (i.e., as the volume of the container). In the quantum treatment, however, the dimensions of the container exert another effect on the range of configurations available to the particles.

Describe how this effect operates, and hence comment on the assumption used in part (i).

(2)

(iii) The rotational constant of the HF molecule is

$$\bar{B} = 20.9560\ \text{cm}^{-1}.$$

Convert this to the equivalent energy in J, and hence evaluate Θ_{rot}, the characteristic rotational temperature. From the accompanying table of values of the function

$$\sum_{J=0}^{\infty}(2J + 1)e^{-xJ(J+1)}, \qquad \text{where} \qquad x = \frac{\Theta_{\text{rot}}}{T}$$

evaluate the rotational partition function for HF at 251.2 K, and compare this with what would be obtained by use of the approximation

$$\sum_{J=0}^{\infty}(2J + 1)e^{-xJ(J+1)} \simeq \int_0^\infty (2J + 1)e^{-xJ(J+1)}\, dJ$$

$$= \frac{1}{x}$$

(3)

[50]

Values of Fundamental Constants:

Boltzmann's Constant:	$k = 1.38066 \times 10^{-23}$ J K^{-1}
Planck's Constant:	$h = 6.62608 \times 10^{-34}$ J s
Avogadro's Number:	$N_A = 6.02214 \times 10^{23}$ mol^{-1}
Velocity of Light:	$c = 2.99793 \times 10^{8}$ m s^{-1}.

Rotational Partition Function

$$z_{rot} = \sum_{J=0}^{\infty} (2J+1) e^{-xJ(J+1)}, \qquad x = \frac{\Theta_{rot}}{T}.$$

x	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0		100.3340	50.3347	33.6687	25.3360	20.3367	17.0040	14.6238	12.8387	11.4505
0.1	10.3401	9.4317	8.6749	8.0345	7.4858	7.0103	6.5943	6.2274	5.9013	5.6096
0.2	5.3472	5.1098	4.8941	4.6972	4.5168	4.3508	4.1977	4.0560	3.9245	3.8021
0.3	3.6879	3.5811	3.4811	3.3871	3.2988	3.2155	3.1369	3.0626	2.9923	2.9256
0.4	2.8623	2.8021	2.7448	2.6902	2.6382	2.5885	2.5410	2.4955	2.4520	2.4103
0.5	2.3703	2.3319	2.2951	2.2596	2.2255	2.1927	2.1611	2.1306	2.1012	2.0729
0.6	2.0455	2.0190	1.9935	1.9688	1.9448	1.9217	1.8993	1.8776	1.8565	1.8361
0.7	1.8164	1.7972	1.7785	1.7604	1.7429	1.7258	1.7092	1.6931	1.6774	1.6622
0.8	1.6473	1.6329	1.6188	1.6051	1.5918	1.5788	1.5661	1.5538	1.5418	1.5301
0.9	1.5186	1.5075	1.4966	1.4860	1.4756	1.4655	1.4556	1.4460	1.4366	1.4274
1.0	1.4184	1.4097	1.4011	1.3927	1.3846	1.3766	1.3688	1.3611	1.3537	1.3464
1.1	1.3392	1.3322	1.3254	1.3187	1.3122	1.3058	1.2996	1.2935	1.2875	1.2816
1.2	1.2759	1.2703	1.2648	1.2594	1.2542	1.2490	1.2440	1.2391	1.2342	1.2295
1.3	1.2249	1.2203	1.2159	1.2116	1.2073	1.2031	1.1991	1.1951	1.1911	1.1873
1.4	1.1836	1.1799	1.1763	1.1727	1.1693	1.1659	1.1626	1.1593	1.1562	1.1530

Statistical Thermodynamics Examination - Marking Scheme

(a)

(i)

$$Z = \sum_{k=0}^{\infty} e^{-\beta E_k}$$

$$\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z}\frac{\partial Z}{\partial \beta} \qquad 1$$

$$= \frac{1}{Z}\sum_{k=0}^{\infty} -E_k e^{-\beta E_k} \qquad 1$$

$$= -\sum_{k=0}^{\infty} E_k \frac{e^{-\beta E_k}}{Z} \qquad 1 \qquad = -\sum_{k=0}^{\infty} E_k P(E_k)$$

$$\therefore \langle E \rangle = \sum_{k=0}^{\infty} E_k \frac{e^{-\beta E_k}}{Z} = -\frac{\partial \ln Z}{\partial \beta}$$

(ii)

$$P(E_k) = \frac{e^{-\beta E_k}}{Z}$$

$$\sum_{k=0}^{\infty} P(E_k) \ln P(E_k) = \sum_{k=0}^{\infty} P(E_k) \ln\left\{\frac{e^{-\beta E_k}}{Z}\right\} \qquad 1$$

$$= \sum_{k=0}^{\infty} P(E_k)\left[-\beta E_k - \ln Z\right] \qquad 1$$

$$= -\beta \sum_{k=0}^{\infty} E_k P(E_k) - \ln Z \sum_{k=0}^{\infty} P(E_k)$$

$$= -\beta U - \ln Z. \qquad 1$$

$$\therefore -k \sum_{k=0}^{\infty} P(E_k) \ln P(E_k) = k \ln Z + \frac{U}{T}$$

1

(b) $Z = e^{\beta\epsilon} + 1 + e^{-\beta\epsilon}$

State	P.F. Term	Probability	Energy Term	Entropy Term
1	2.718281828	0.665240956	−0.665240956	0.271156181
2	1.000000000	0.244728~~385~~471	0	0.344481256
3	0.367879441	0.090030~~542~~573	+0.090030573	0.216758145
Sum	4.086161270	1.000000000	~~−0.575210383~~ −0.575210383	0.832395582

Particle partition function = 4.086161270

average energy per particle = −0.575210383

entropy ÷ k = 0.832395582

If $\beta\epsilon = 0.01$ the partition function is 3.000100001

The probabilities of the states are nearly the same

0.336672167
0.333322222
0.330005611

The entropy will greater:

0.366516680
0.366203000
0.365859276
1.098578956

The energy is

−0.003366722
0
0.003300056
−0.000066666

i.e. closer to zero

(c)

(i) $$\eta(v) = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(-\frac{mv^2}{2kT}\right)$$

$v = 500\ \mathrm{m\,s^{-1}}$ $\quad T = 300\ \mathrm{K}$ $\quad m = \dfrac{16.04\ \mathrm{g\,mol^{-1}}}{6.02214\times10^{23}\ \mathrm{mol^{-1}}}$

$= 2.664\times10^{-26}\ \mathrm{kg}$

$\dfrac{mv^2}{2kT} =$ ~~0.80396~~ 0.8040

$$\left(\frac{m}{2\pi kT}\right)^{3/2} = 1.036\times10^{-9}$$

$$\eta(v) = 4\pi \times (500)^2 \times 1.036\times10^{-9} \times \exp(-0.8040)$$

$$= 1.456\times10^{-3}$$

$$\therefore \eta(v)\,\delta v = (1.456\times10^{-3}\ \mathrm{s\,m^{-1}}) \times (1\ \mathrm{m\,s^{-1}})$$

$= 1.456\times10^{-3}$ = probability.

(ii) $$\langle v\rangle = \int_0^\infty v\,\eta(v)\,dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^3 \exp\left(-\frac{mv^2}{2kT}\right) dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2kT}{m}\right)^2 \cdot \frac{1}{2}$$

$$= \frac{2\pi}{(\sqrt{\pi})^3}\left(\frac{2kT}{m}\right)^{\frac{1}{2}} = \left(\frac{8kT}{\pi m}\right)^{\frac{1}{2}}$$

$$\langle v^2\rangle = \int_0^\infty v^2\,\eta(v)\,dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^4 \exp\left(-\frac{mv^2}{2kT}\right) dv$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\cdot\frac{3\sqrt{\pi}}{8}\cdot\left(\frac{2kT}{m}\right)^{5/2}$$

$$= \frac{12\cancel{\pi^{3/2}}}{8\cancel{\pi^{3/2}}}\cdot\left(\frac{m}{2kT}\right)^{3/2}\cdot\left(\frac{2kT}{m}\right)^{5/2}$$

$$= \frac{3kT}{m}$$

$$\therefore V_{rms} = \sqrt{\frac{3kT}{m}}$$

(d) (i) $$z_t = \int_0^\infty\int_0^\infty\int_0^\infty \exp\left(-\frac{\varepsilon_{n_1n_2n_3}}{kT}\right)dn_1\,dn_2\,dn_3$$

$$= \left(\int_0^\infty \exp\left(-\frac{n_1^2h^2}{8ma^2kT}\right)dn_1\right)\left(\int_0^\infty \exp\left(-\frac{n_2^2h^2}{8mb^2kT}\right)dn_2\right)$$

$$\times\left(\int_0^\infty \exp\left(-\frac{n_3^2h^2}{8mc^2kT}\right)dn_3\right)$$

$$= \frac{1}{2}\sqrt{\frac{\pi 8ma^2kT}{h^2}}\cdot\frac{1}{2}\sqrt{\frac{\pi 8mb^2kT}{h^2}}\cdot\frac{1}{2}\sqrt{\frac{\pi 8mc^2kT}{h^2}}$$

$$= \cancel{\frac{abc}{8h^3}}\cdot \cancel{=}\ \frac{abc}{h^3}\cdot(2\pi mkT)^{3/2}$$

(ii) The dimensions of the container also affect the separation between the energy levels, e.g. through

$$\varepsilon = \frac{h^2}{8m}\left(\frac{n_1^2}{a^2}+\frac{n_2^2}{b^2}+\frac{n_3^2}{c^2}\right)$$

(iii) $$\bar{B} = 20.9560\ \text{cm}^{-1} = 2095.60\ \text{m}^{-1}$$

$$B = hc\bar{B}$$

$$= (6.62608\times10^{-34}\ \text{Js})\times(2.99793\times10^{8}\ \text{ms}^{-1})$$

$$\times\ (2095.60\ \text{m}^{-1})$$

$$= 4.163\times10^{-22}\ \text{J}$$

$$\Theta_{rot} = \frac{B}{k} = 30.15\ K.$$

At 251.2, $\frac{\Theta_{rot}}{T} = \frac{30.15}{251.2} = 0.12$. From table, $z_{rot} = 8.6749$; with the approximation $z_{rot} = \frac{1}{0.12} = 8.3333$

Approximating polynomial for $\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-t^2}\,dt$

$$\operatorname{erf} x_0 = 1 - \frac{1}{[1 + a_1x + a_2x^2 + \dots + a_6x^6]^{16}} + \varepsilon(x)$$

$$|\varepsilon(x)| \le 3\times10^{-7}$$

$a_1 = 0.0705230784$ $\quad 7.0523078 4\times10^{-2}$

$a_2 = 0.0422820123$ $\quad 4.22820123\times10^{-2}$

$a_3 = 0.0092705272$ $\quad 9.2705272\times10^{-3}$

$a_4 = 0.0001520143$ $\quad 1.520143\times10^{-4}$

$a_5 = 0.0002765672$ $\quad 2.765672\times10^{-4}$

$a_6 = 0.0000430638$ $\quad 4.30638\times10^{-5}$

$\Gamma(n+1) = n\Gamma(n)$

$\Gamma(\tfrac{3}{2}) = \tfrac{1}{2}\Gamma(\tfrac{1}{2})$

$$\eta(v) = 4\pi v^2\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}$$

$$\int_V^\infty \eta(v)\,dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_V^\infty v^2 e^{-mv^2/2kT}\,dv$$

$E = \frac{1}{2}mv^2 \quad v = \sqrt{E/2m} \quad v^2 = E/2m$

$dE = \cancel{2}mv\,dv \quad dv = \frac{dE}{\cancel{2}mv} = \frac{1}{\cancel{2}m}\cdot\frac{dE}{\sqrt{E/2m}} = \frac{\sqrt{2}\,dE}{\cancel{2}\sqrt{mE}}$

$$\therefore \int_V^\infty \eta(v)\,dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_{\sqrt{E/2m}}^\infty \frac{E}{2m}\cdot e^{-E/kT}\cdot\frac{\sqrt{2}\,dE}{\sqrt{m}\sqrt{E}}$$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{\sqrt{2}}{2m^{3/2}}\int_{\sqrt{E/2m}}^\infty E^{\frac{1}{2}}e^{-E/kT}\,dE$$

$\cancel{4\pi}\cdot\frac{1}{(2\pi)^{3/2}}\cdot\frac{1}{\sqrt{2}}$

$= \frac{1}{2\sqrt{\pi}}$

$$= 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\cdot\frac{1}{2}\left(\frac{kT}{m}\right)^{3/2}\sqrt{2}\int_{\sqrt{E/2m}}^\infty\left(\frac{E}{kT}\right)^{\frac{1}{2}}e^{-E/kT}\,\frac{dE}{kT}$$

$2\cdot\frac{2\pi}{(2\pi)^{3/2}}\cdot\frac{1}{\sqrt{2}} = \frac{\sqrt{2}}{\sqrt{2\pi}} = \frac{1}{\sqrt{\pi}}$

$$= \frac{\cancel{2}}{\sqrt{\pi}}\int_{\sqrt{E/2mkT}}^\infty t^{\frac{1}{2}}e^{-t}\,dt$$

$E = 0$: integral $= \frac{1}{\cancel{2}\sqrt{\pi}}\int_0^\infty t^{\frac{1}{2}}e^{-t}\,dt = \frac{1}{\sqrt{\pi}}\Gamma\left(\frac{3}{2}\right) =$

$\sqrt{kT/m} = v_0 \;.\; kT = mv_0^2$

$$\operatorname{erf} x = \sqrt{\frac{2}{\pi}}\int_0^x e^{-t^2}dt \quad = \quad \frac{1}{\sqrt{2\pi}}\int_0^{x/\sqrt{2}} e^{-t^2/2}\,dt$$

$$\cancel{\int u^2 e^{-u^2/2}du =} \qquad \frac{1}{\sqrt{2\pi}}\int_0^x e^{-u^2/2}du \qquad t = \frac{u}{\sqrt{2}} \quad \frac{du}{\sqrt{2}} = dt$$

$$= \frac{\sqrt{2}}{\sqrt{2\pi}}\int_0^x e^{-u^2/2}\frac{du}{\sqrt{2}} = \frac{\sqrt{2}}{\sqrt{2\pi}}\int_0^{x/\sqrt{2}} e^{-t^2}dt$$

$$= \sqrt{\frac{2}{\pi}}\int_0^{x/\sqrt{2}} e^{-t^2}dt$$

$$\int_0^x u^2 e^{-u^2/2}du \qquad \frac{d}{du}\left(e^{-u^2/2}\right) = -ue^{-u^2/2} \qquad = \operatorname{erf}\left(\frac{x}{\sqrt{2}}\right)$$

$$= \int_0^x \left(ue^{-u^2/2}\right)u\,du$$

$$= \quad - \int_0^x u\frac{d}{du}\left(e^{-u^2/2}\right)du \qquad \frac{1}{\sqrt{2\pi}}\int_x^\infty e^{-u^2/2}du$$

$$= \quad -\left\{\left[ue^{-u^2/2}\right]_0^x - \int_0^x e^{-u^2/2}du\right\} \qquad = \operatorname{erfc}\left(\frac{x}{\sqrt{2}}\right)$$

$$= \quad -\left(xe^{-x^2/2} - 0\right) + \int_0^x e^{-u^2/2}du$$

$$= \quad -xe^{-x^2/2} + \sqrt{2\pi}\operatorname{erf}\left(x/\sqrt{2}\right)$$

$$\int_v^\infty g(v)\,dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_v^\infty v^2 e^{-mv^2/2kT}dv$$

$$\text{Put} \quad u = v\sqrt{\frac{m}{kT}} \qquad du = \sqrt{\frac{m}{kT}}dv \qquad dv = \sqrt{\frac{kT}{m}}du$$

$$u^2 = v^2\frac{m}{kT} \qquad v^2 = \frac{kT}{m}u^2$$

$$\therefore \text{integral} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\left(\frac{kT}{m}\right)^{3/2}\int_{v\sqrt{\frac{m}{kT}}}^\infty u^2 e^{-u^2/2}du$$

$$\frac{4\pi}{(2\pi)^{3/2}} = \frac{2\cdot 2\pi}{(2\pi)^{3/2}} = \sqrt{\frac{2}{\pi}}$$

$$= \frac{4\pi}{(2\pi)^{3/2}}\int_{v\sqrt{m/kT}}^\infty u^2 e^{-u^2/2}du \qquad \frac{v}{v_m} = v\sqrt{\frac{2kT}{m}}$$

$$= \sqrt{\frac{2}{\pi}}\int_{v\sqrt{m/kT}}^\infty u^2 e^{-u^2/2}du \qquad v\sqrt{\frac{2m}{\pi kT}} = v\sqrt{\frac{4m}{2\pi kT}} = v\sqrt{\frac{m}{2kT}}\sqrt{\frac{4}{\pi}}$$

$$= \frac{2}{\sqrt{\pi}}\cdot\frac{v}{v_m}$$

$$= -\sqrt{\frac{2}{\pi}}\left\{\left[ue^{-u^2/2}\right]_{v\sqrt{\frac{m}{kT}}}^\infty - \int_{v\sqrt{\frac{m}{kT}}}^\infty e^{-u^2/2}du\right\}$$

$$= \sqrt{\frac{2}{\pi}}\cdot v\sqrt{\frac{m}{kT}}e^{-mv^2/2kT} + \sqrt{\frac{2}{\pi}}\int_{v\sqrt{\frac{m}{kT}}}^\infty e^{-u^2/2}du = v\sqrt{\frac{2m}{\pi kT}}e^{-mv^2/2kT} + \operatorname{erfc}\left(v\sqrt{\frac{m}{2kT}}\right)$$

$$= \frac{2}{\sqrt{\pi}}\frac{v}{v_m}e^{-(v/v_m)^2} + 2\operatorname{erfc}\left(\frac{v}{v_m}\right)$$

THE NORMAL PROBABILITY FUNCTION AND RELATED FUNCTIONS

This table gives values of:

a) $f(x)$ = the probability density of a standardized random variable

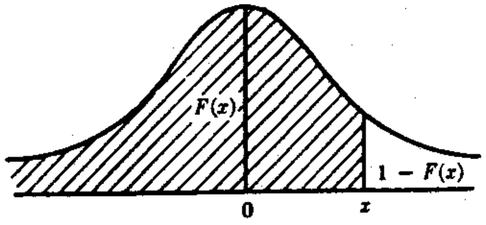
$$= \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}x^2}$$

For negative values of x, one uses the fact that $f(-x) = f(x)$.

b) $F(x)$ = the cumulative distribution function of a standardized normal random variable

$$= \int_{-\infty}^{x} \frac{1}{\sqrt{2\pi}} e^{-\frac{1}{2}t^2}\,dt$$

For negative values of x, one uses the relationship $F(-x) = 1 - F(x)$. Values of x corresponding to a few special values of $F(x)$ are given in a separate table following the main table. (See page 560.)



c) $f'(x)$ = the first derivative of $f(x)$ with respect to x

$$= -\frac{x}{\sqrt{2\pi}} e^{-\frac{1}{2}x^2} = -xf(x)$$

d) $f''(x)$ = the second derivative of $f(x)$ with respect to x

$$= \frac{(x^2-1)}{\sqrt{2\pi}} e^{-\frac{1}{2}x^2} = (x^2-1)f(x)$$

e) $f'''(x)$ = the third derivative of $f(x)$ with respect to x

$$= \frac{3x - x^3}{\sqrt{2\pi}} e^{-\frac{1}{2}x^2} = (3x - x^3)f(x)$$

f) $f^{iv}(x)$ = the fourth derivative of $f(x)$ with respect to x

$$= \frac{x^4 - 6x^2 + 3}{\sqrt{2\pi}} e^{-\frac{1}{2}x^2} = (x^4 - 6x^2 + 3)f(x)$$

It should be noted that other probability integrals can be evaluated by the use of these tables. For example,

$$\int_0^x f(t)dt = \tfrac{1}{2}\,\mathrm{erf}\left(\frac{x}{\sqrt{2}}\right),$$

where $\mathrm{erf}\left(\frac{x}{\sqrt{2}}\right)$ represents the error function associated with the normal curve.

To evaluate erf (2.3) one proceeds as follows: Since $\frac{x}{\sqrt{2}} = 2.3$, one finds $x = (2.3)(\sqrt{2}) = 3.25$. In the entry opposite $x = 3.25$, the value 0.9994 is given. Subtracting 0.5000 from the tabular value, one finds the value 0.4994. Thus erf (2.3) = 2(0.4994) = 0.9988.

NORMAL DISTRIBUTION AND RELATED FUNCTIONS

x	$F(x)$	$1 - F(x)$	$f(x)$	$f'(x)$	$f''(x)$	$f'''(x)$	$f^{iv}(x)$
.00	.5000	.5000	.3989	−.0000	−.3989	.0000	1.1968
.01	.5040	.4960	.3989	−.0040	−.3989	.0120	1.1965
.02	.5080	.4920	.3989	−.0080	−.3987	.0239	1.1956
.03	.5120	.4880	.3988	−.0120	−.3984	.0359	1.1941
.04	.5160	.4840	.3986	−.0159	−.3980	.0478	1.1920
.05	.5199	.4801	.3984	−.0199	−.3975	.0597	1.1894
.06	.5239	.4761	.3982	−.0239	−.3968	.0716	1.1861
.07	.5279	.4721	.3980	−.0279	−.3960	.0834	1.1822
.08	.5319	.4681	.3977	−.0318	−.3951	.0952	1.1778
.09	.5359	.4641	.3973	−.0358	−.3941	.1070	1.1727
.10	.5398	.4602	.3970	−.0397	−.3930	.1187	1.1671
.11	.5438	.4562	.3965	−.0436	−.3917	.1303	1.1609
.12	.5478	.4522	.3961	−.0475	−.3904	.1419	1.1541
.13	.5517	.4483	.3956	−.0514	−.3889	.1534	1.1468
.14	.5557	.4443	.3951	−.0553	−.3873	.1648	1.1389
.15	.5596	.4404	.3945	−.0592	−.3856	.1762	1.1304
.16	.5636	.4364	.3939	−.0630	−.3838	.1874	1.1214
.17	.5675	.4325	.3932	−.0668	−.3819	.1986	1.1118
.18	.5714	.4286	.3925	−.0707	−.3798	.2097	1.1017
.19	.5753	.4247	.3918	−.0744	−.3777	.2206	1.0911
.20	.5793	.4207	.3910	−.0782	−.3754	.2315	1.0799
.21	.5832	.4168	.3902	−.0820	−.3730	.2422	1.0682
.22	.5871	.4129	.3894	−.0857	−.3706	.2529	1.0560
.23	.5910	.4090	.3885	−.0894	−.3680	.2634	1.0434
.24	.5948	.4052	.3876	−.0930	−.3653	.2737	1.0302
.25	.5987	.4013	.3867	−.0967	−.3625	.2840	1.0165
.26	.6026	.3974	.3857	−.1003	−.3596	.2941	1.0024
.27	.6064	.3936	.3847	−.1039	−.3566	.3040	0.9878
.28	.6103	.3897	.3836	−.1074	−.3535	.3138	0.9727
.29	.6141	.3859	.3825	−.1109	−.3504	.3235	0.9572
.30	.6179	.3821	.3814	−.1144	−.3471	.3330	0.9413
.31	.6217	.3783	.3802	−.1179	−.3437	.3423	0.9250
.32	.6255	.3745	.3790	−.1213	−.3402	.3515	0.9082
.33	.6293	.3707	.3778	−.1247	−.3367	.3605	0.8910
.34	.6331	.3669	.3765	−.1280	−.3330	.3693	0.8735
.35	.6368	.3632	.3752	−.1313	−.3293	.3779	0.8556
.36	.6406	.3594	.3739	−.1346	−.3255	.3864	0.8373
.37	.6443	.3557	.3725	−.1378	−.3216	.3947	0.8186
.38	.6480	.3520	.3712	−.1410	−.3176	.4028	0.7996
.39	.6517	.3483	.3697	−.1442	−.3135	.4107	0.7803
.40	.6554	.3446	.3683	−.1473	−.3094	.4184	0.7607
.41	.6591	.3409	.3668	−.1504	−.3051	.4259	0.7408
.42	.6628	.3372	.3653	−.1534	−.3008	.4332	0.7206
.43	.6664	.3336	.3637	−.1564	−.2965	.4403	0.7001
.44	.6700	.3300	.3621	−.1593	−.2920	.4472	0.6793
.45	.6736	.3264	.3605	−.1622	−.2875	.4539	0.6583
.46	.6772	.3228	.3589	−.1651	−.2830	.4603	0.6371
.47	.6808	.3192	.3572	−.1679	−.2783	.4666	0.6156
.48	.6844	.3156	.3555	−.1707	−.2736	.4727	0.5940
.49	.6879	.3121	.3538	−.1734	−.2689	.4785	0.5721
.50	.6915	.3085	.3521	−.1760	−.2641	.4841	0.5501

NORMAL DISTRIBUTION AND RELATED FUNCTIONS

x	$F(x)$	$1 - F(x)$	$f(x)$	$f'(x)$	$f''(x)$	$f'''(x)$	$f^{iv}(x)$
.50	.6915	.3085	.3521	−.1760	−.2641	.4841	.5501
.51	.6950	.3050	.3503	−.1787	−.2592	.4895	.5279
.52	.6985	.3015	.3485	−.1812	−.2543	.4947	.5056
.53	.7019	.2981	.3467	−.1837	−.2493	.4996	.4831
.54	.7054	.2946	.3448	−.1862	−.2443	.5043	.4605
.55	.7088	.2912	.3429	−.1886	−.2392	.5088	.4378
.56	.7123	.2877	.3410	−.1920	−.2341	.5131	.4150
.57	.7157	.2843	.3391	−.1933	−.2289	.5171	.3921
.58	.7190	.2810	.3372	−.1956	−.2238	.5209	.3691
.59	.7224	.2776	.3352	−.1978	−.2185	.5245	.3461
.60	.7257	.2743	.3332	−.1999	−.2133	.5278	.3231
.61	.7291	.2709	.3312	−.2020	−.2080	.5309	.3000
.62	.7324	.2676	.3292	−.2041	−.2027	.5338	.2770
.63	.7357	.2643	.3271	−.2061	−.1973	.5365	.2539
.64	.7389	.2611	.3251	−.2080	−.1919	.5389	.2309
.65	.7422	.2578	.3230	−.2099	−.1865	.5411	.2078
.66	.7454	.2546	.3209	−.2118	−.1811	.5431	.1849
.67	.7486	.2514	.3187	−.2136	−.1757	.5448	.1620
.68	.7517	.2483	.3166	−.2153	−.1702	.5463	.1391
.69	.7549	.2451	.3144	−.2170	−.1647	.5476	.1164
.70	.7580	.2420	.3123	−.2186	−.1593	.5486	.0937
.71	.7611	.2389	.3101	−.2201	−.1538	.5495	.0712
.72	.7642	.2358	.3079	−.2217	−.1483	.5501	.0487
.73	.7673	.2327	.3056	−.2231	−.1428	.5504	.0265
.74	.7704	.2296	.3034	−.2245	−.1373	.5506	.0043
.75	.7734	.2266	.3011	−.2259	−.1318	.5505	−.0176
.76	.7764	.2236	.2989	−.2271	−.1262	.5502	−.0394
.77	.7794	.2206	.2966	−.2284	−.1207	.5497	−.0611
.78	.7823	.2177	.2943	−.2296	−.1153	.5490	−.0825
.79	.7852	.2148	.2920	−.2307	−.1098	.5481	−.1037
.80	.7881	.2119	.2897	−.2318	−.1043	.5469	−.1247
.81	.7910	.2090	.2874	−.2328	−.0988	.5456	−.1455
.82	.7939	.2061	.2850	−.2337	−.0934	.5440	−.1660
.83	.7967	.2033	.2827	−.2346	−.0880	.5423	−.1862
.84	.7995	.2005	.2803	−.2355	−.0825	.5403	−.2063
.85	.8023	.1977	.2780	−.2363	−.0771	.5381	−.2260
.86	.8051	.1949	.2756	−.2370	−.0718	.5358	−.2455
.87	.8078	.1922	.2732	−.2377	−.0664	.5332	−.2646
.88	.8106	.1894	.2709	−.2384	−.0611	.5305	−.2835
.89	.8133	.1867	.2685	−.2389	−.0558	.5276	−.3021
.90	.8159	.1841	.2661	−.2395	−.0506	.5245	−.3203
.91	.8186	.1814	.2637	−.2400	−.0453	.5212	−.3383
.92	.8212	.1788	.2613	−.2404	−.0401	.5177	−.3559
.93	.8238	.1762	.2589	−.2408	−.0350	.5140	−.3731
.94	.8264	.1736	.2565	−.2411	−.0299	.5102	−.3901
.95	.8289	.1711	.2541	−.2414	−.0248	.5062	−.4066
.96	.8315	.1685	.2516	−.2416	−.0197	.5021	−.4228
.97	.8340	.1660	.2492	−.2417	−.0147	.4978	−.4387
.98	.8365	.1635	.2468	−.2419	−.0098	.4933	−.4541
.99	.8389	.1611	.2444	−.2420	−.0049	.4887	−.4692
1.00	.8413	.1587	.2420	−.2420	.0000	.4839	−.4839

NORMAL DISTRIBUTION AND RELATED FUNCTIONS

x	$F(x)$	$1 - F(x)$	$f(x)$	$f'(x)$	$f''(x)$	$f'''(x)$	$f^{iv}(x)$
1.00	.8413	.1587	.2420	−.2420	.0000	.4839	−.4839
1.01	.8438	.1562	.2396	−.2420	.0048	.4790	−.4983
1.02	.8461	.1539	.2371	−.2419	.0096	.4740	−.5122
1.03	.8485	.1515	.2347	−.2418	.0143	.4688	−.5257
1.04	.8508	.1492	.2323	−.2416	.0190	.4635	−.5389
1.05	.8531	.1469	.2299	−.2414	.0236	.4580	−.5516
1.06	.8554	.1446	.2275	−.2411	.0281	.4524	−.5639
1.07	.8577	.1423	.2251	−.2408	.0326	.4467	−.5758
1.08	.8599	.1401	.2227	−.2405	.0371	.4409	−.5873
1.09	.8621	.1379	.2203	−.2401	.0414	.4350	−.5984
1.10	.8643	.1357	.2179	−.2396	.0458	.4290	−.6091
1.11	.8665	.1335	.2155	−.2392	.0500	.4228	−.6193
1.12	.8686	.1314	.2131	−.2386	.0542	.4166	−.6292
1.13	.8708	.1292	.2107	−.2381	.0583	.4102	−.6386
1.14	.8729	.1271	.2083	−.2375	.0624	.4038	−.6476
1.15	.8749	.1251	.2059	−.2368	.0664	.3973	−.6561
1.16	.8770	.1230	.2036	−.2361	.0704	.3907	−.6643
1.17	.8790	.1210	.2012	−.2354	.0742	.3840	−.6720
1.18	.8810	.1190	.1989	−.2347	.0780	.3772	−.6792
1.19	.8830	.1170	.1965	−.2339	.0818	.3704	−.6861
1.20	.8849	.1151	.1942	−.2330	.0854	.3635	−.6926
1.21	.8869	.1131	.1919	−.2322	.0890	.3566	−.6986
1.22	.8888	.1112	.1895	−.2312	.0926	.3496	−.7042
1.23	.8907	.1093	.1872	−.2303	.0960	.3425	−.7094
1.24	.8925	.1075	.1849	−.2293	.0994	.3354	−.7141
1.25	.8944	.1056	.1826	−.2283	.1027	.3282	−.7185
1.26	.8962	.1038	.1804	−.2273	.1060	.3210	−.7224
1.27	.8980	.1020	.1781	−.2262	.1092	.3138	−.7259
1.28	.8997	.1003	.1758	−.2251	.1123	.3065	−.7291
1.29	.9015	.0985	.1736	−.2240	.1153	.2992	−.7318
1.30	.9032	.0968	.1714	−.2228	.1182	.2918	−.7341
1.31	.9049	.0951	.1691	−.2216	.1211	.2845	−.7361
1.32	.9066	.0934	.1669	−.2204	.1239	.2771	−.7376
1.33	.9082	.0918	.1647	−.2191	.1267	.2697	−.7388
1.34	.9099	.0901	.1626	−.2178	.1293	.2624	−.7395
1.35	.9115	.0885	.1604	−.2165	.1319	.2550	−.7399
1.36	.9131	.0869	.1582	−.2152	.1344	.2476	−.7400
1.37	.9147	.0853	.1561	−.2138	.1369	.2402	−.7396
1.38	.9162	.0838	.1539	−.2125	.1392	.2328	−.7389
1.39	.9177	.0823	.1518	−.2110	.1415	.2254	−.7378
1.40	.9192	.0808	.1497	−.2096	.1437	.2180	−.7364
1.41	.9207	.0793	.1476	−.2082	.1459	.2107	−.7347
1.42	.9222	.0778	.1456	−.2067	.1480	.2033	−.7326
1.43	.9236	.0764	.1435	−.2052	.1500	.1960	−.7301
1.44	.9251	.0749	.1415	−.2037	.1519	.1887	−.7274
1.45	.9265	.0735	.1394	−.2022	.1537	.1815	−.7243
1.46	.9279	.0721	.1374	−.2006	.1555	.1742	−.7209
1.47	.9292	.0708	.1354	−.1991	.1572	.1670	−.7172
1.48	.9306	.0694	.1334	−.1975	.1588	.1599	−.7132
1.49	.9319	.0681	.1315	−.1959	.1604	.1528	−.7089
1.50	.9332	.0668	.1295	−.1943	.1619	.1457	−.7043

NORMAL DISTRIBUTION AND RELATED FUNCTIONS

x	$F(x)$	$1 - F(x)$	$f(x)$	$f'(x)$	$f''(x)$	$f'''(x)$	$f^{iv}(x)$
1.50	.9332	.0668	.1295	−.1943	.1619	.1457	−.7043
1.51	.9345	.0655	.1276	−.1927	.1633	.1387	−.6994
1.52	.9357	.0643	.1257	−.1910	.1647	.1317	−.6942
1.53	.9370	.0630	.1238	−.1894	.1660	.1248	−.6888
1.54	.9382	.0618	.1219	−.1877	.1672	.1180	−.6831
1.55	.9394	.0606	.1200	−.1860	.1683	.1111	−.6772
1.56	.9406	.0594	.1182	−.1843	.1694	.1044	−.6710
1.57	.9418	.0582	.1163	−.1826	.1704	.0977	−.6646
1.58	.9429	.0571	.1145	−.1809	.1714	.0911	−.6580
1.59	.9441	.0559	.1127	−.1792	.1722	.0846	−.6511
1.60	.9452	.0548	.1109	−.1775	.1730	.0781	−.6441
1.61	.9463	.0537	.1092	−.1757	.1738	.0717	−.6368
1.62	.9474	.0526	.1074	−.1740	.1745	.0654	−.6293
1.63	.9484	.0516	.1057	−.1723	.1751	.0591	−.6216
1.64	.9495	.0505	.1040	−.1705	.1757	.0529	−.6138
1.65	.9505	.0495	.1023	−.1687	.1762	.0468	−.6057
1.66	.9515	.0485	.1006	−.1670	.1766	.0408	−.5975
1.67	.9525	.0475	.0989	−.1652	.1770	.0349	−.5891
1.68	.9535	.0465	.0973	−.1634	.1773	.0290	−.5806
1.69	.9545	.0455	.0957	−.1617	.1776	.0233	−.5720
1.70	.9554	.0446	.0940	−.1599	.1778	.0176	−.5632
1.71	.9564	.0436	.0925	−.1581	.1779	.0120	−.5542
1.72	.9573	.0427	.0909	−.1563	.1780	.0065	−.5452
1.73	.9582	.0418	.0893	−.1546	.1780	.0011	−.5360
1.74	.9591	.0409	.0878	−.1528	.1780	−.0042	−.5267
1.75	.9599	.0401	.0863	−.1510	.1780	−.0094	−.5173
1.76	.9608	.0392	.0848	−.1492	.1778	−.0146	−.5079
1.77	.9616	.0384	.0833	−.1474	.1777	−.0196	−.4983
1.78	.9625	.0375	.0818	−.1457	.1774	−.0245	−.4887
1.79	.9633	.0367	.0804	−.1439	.1772	−.0294	−.4789
1.80	.9641	.0359	.0790	−.1421	.1769	−.0341	−.4692
1.81	.9649	.0351	.0775	−.1403	.1765	−.0388	−.4593
1.82	.9656	.0344	.0761	−.1386	.1761	−.0433	−.4494
1.83	.9664	.0336	.0748	−.1368	.1756	−.0477	−.4395
1.84	.9671	.0329	.0734	−.1351	.1751	−.0521	−.4295
1.85	.9678	.0322	.0721	−.1333	.1746	−.0563	−.4195
1.86	.9686	.0314	.0707	−.1316	.1740	−.0605	−.4095
1.87	.9693	.0307	.0694	−.1298	.1734	−.0645	−.3995
1.88	.9699	.0301	.0681	−.1281	.1727	−.0685	−.3894
1.89	.9706	.0294	.0669	−.1264	.1720	−.0723	−.3793
1.90	.9713	.0287	.0656	−.1247	.1713	−.0761	−.3693
1.91	.9719	.0281	.0644	−.1230	.1705	−.0797	−.3592
1.92	.9726	.0274	.0632	−.1213	.1697	−.0832	−.3492
1.93	.9732	.0268	.0620	−.1196	.1688	−.0867	−.3392
1.94	.9738	.0262	.0608	−.1179	.1679	−.0900	−.3292
1.95	.9744	.0256	.0596	−.1162	.1670	−.0933	−.3192
1.96	.9750	.0250	.0584	−.1145	.1661	−.0964	−.3093
1.97	.9756	.0244	.0573	−.1129	.1651	−.0994	−.2994
1.98	.9761	.0239	.0562	−.1112	.1641	−.1024	−.2895
1.99	.9767	.0233	.0551	−.1096	.1630	−.1052	−.2797
2.00	.9772	.0228	.0540	−.1080	.1620	−.1080	−.2700

NORMAL DISTRIBUTION AND RELATED FUNCTIONS

x	$F(x)$	$1 - F(x)$	$f(x)$	$f'(x)$	$f''(x)$	$f'''(x)$	$f^{iv}(x)$
2.00	.9773	.0227	.0540	−.1080	.1620	−.1080	−.2700
2.01	.9778	.0222	.0529	−.1064	.1609	−.1106	−.2603
2.02	.9783	.0217	.0519	−.1048	.1598	−.1132	−.2506
2.03	.9788	.0212	.0508	−.1032	.1586	−.1157	−.2411
2.04	.9793	.0207	.0498	−.1016	.1575	−.1180	−.2316
2.05	.9798	.0202	.0488	−.1000	.1563	−.1203	−.2222
2.06	.9803	.0197	.0478	−.0985	.1550	−.1225	−.2129
2.07	.9808	.0192	.0468	−.0969	.1538	−.1245	−.2036
2.08	.9812	.0188	.0459	−.0954	.1526	−.1265	−.1945
2.09	.9817	.0183	.0449	−.0939	.1513	−.1284	−.1854
2.10	.9821	.0179	.0440	−.0924	.1500	−.1302	−.1765
2.11	.9826	.0174	.0431	−.0909	.1487	−.1320	−.1676
2.12	.9830	.0170	.0422	−.0894	.1474	−.1336	−.1588
2.13	.9834	.0166	.0413	−.0879	.1460	−.1351	−.1502
2.14	.9838	.0162	.0404	−.0865	.1446	−.1366	−.1416
2.15	.9842	.0158	.0396	−.0850	.1433	−.1380	−.1332
2.16	.9846	.0154	.0387	−.0836	.1419	−.1393	−.1249
2.17	.9850	.0150	.0379	−.0822	.1405	−.1405	−.1167
2.18	.9854	.0146	.0371	−.0808	.1391	−.1416	−.1086
2.19	.9857	.0143	.0363	−.0794	.1377	−.1426	−.1006
2.20	.9861	.0139	.0355	−.0780	.1362	−.1436	−.0927
2.21	.9864	.0136	.0347	−.0767	.1348	−.1445	−.0850
2.22	.9868	.0132	.0339	−.0754	.1333	−.1453	−.0774
2.23	.9871	.0129	.0332	−.0740	.1319	−.1460	−.0700
2.24	.9875	.0125	.0325	−.0727	.1304	−.1467	−.0626
2.25	.9878	.0122	.0317	−.0714	.1289	−.1473	−.0554
2.26	.9881	.0119	.0310	−.0701	.1275	−.1478	−.0484
2.27	.9884	.0116	.0303	−.0689	.1260	−.1483	−.0414
2.28	.9887	.0113	.0297	−.0676	.1245	−.1486	−.0346
2.29	.9890	.0110	.0290	−.0664	.1230	−.1490	−.0279
2.30	.9893	.0107	.0283	−.0652	.1215	−.1492	−.0214
2.31	.9896	.0104	.0277	−.0639	.1200	−.1494	−.0150
2.32	.9898	.0102	.0270	−.0628	.1185	−.1495	−.0088
2.33	.9901	.0099	.0264	−.0616	.1170	−.1496	−.0027
2.34	.9904	.0096	.0258	−.0604	.1155	−.1496	.0033
2.35	.9906	.0094	.0252	−.0593	.1141	−.1495	.0092
2.36	.9909	.0091	.0246	−.0581	.1126	−.1494	.0149
2.37	.9911	.0089	.0241	−.0570	.1111	−.1492	.0204
2.38	.9913	.0087	.0235	−.0559	.1096	−.1490	.0258
2.39	.9916	.0084	.0229	−.0548	.1081	−.1487	.0311
2.40	.9918	.0082	.0224	−.0538	.1066	−.1483	.0362
2.41	.9920	.0080	.0219	−.0527	.1051	−.1480	.0412
2.42	.9922	.0078	.0213	−.0516	.1036	−.1475	.0461
2.43	.9925	.0075	.0208	−.0506	.1022	−.1470	.0508
2.44	.9927	.0073	.0203	−.0496	.1007	−.1465	.0554
2.45	.9929	.0071	.0198	−.0486	.0992	−.1459	.0598
2.46	.9931	.0069	.0194	−.0476	.0978	−.1453	.0641
2.47	.9932	.0068	.0189	−.0467	.0963	−.1446	.0683
2.48	.9934	.0066	.0184	−.0457	.0949	−.1439	.0723
2.49	.9936	.0064	.0180	−.0448	.0935	−.1432	.0762
2.50	.9938	.0062	.0175	−.0438	.0920	−.1424	.0800

NORMAL DISTRIBUTION AND RELATED FUNCTIONS

x	$F(x)$	$1 - F(x)$	$f(x)$	$f'(x)$	$f''(x)$	$f'''(x)$	$f^{iv}(x)$
2.50	.9938	.0062	.0175	−.0438	.0920	−.1424	.0800
2.51	.9940	.0060	.0171	−.0429	.0906	−.1416	.0836
2.52	.9941	.0059	.0167	−.0420	.0892	−.1408	.0871
2.53	.9943	.0057	.0163	−.0411	.0878	−.1399	.0905
2.54	.9945	.0055	.0158	−.0403	.0864	−.1389	.0937
2.55	.9946	.0054	.0155	−.0394	.0850	−.1380	.0968
2.56	.9948	.0052	.0151	−.0386	.0836	−.1370	.0998
2.57	.9949	.0051	.0147	−.0377	.0823	−.1360	.1027
2.58	.9951	.0049	.0143	−.0369	.0809	−.1350	.1054
2.59	.9952	.0048	.0139	−.0361	.0796	−.1339	.1080
2.60	.9953	.0047	.0136	−.0353	.0782	−.1328	.1106
2.61	.9955	.0045	.0132	−.0345	.0769	−.1317	.1129
2.62	.9956	.0044	.0129	−.0338	.0756	−.1305	.1152
2.63	.9957	.0043	.0126	−.0330	.0743	−.1294	.1173
2.64	.9959	.0041	.0122	−.0323	.0730	−.1282	.1194
2.65	.9960	.0040	.0119	−.0316	.0717	−.1270	.1213
2.66	.9961	.0039	.0116	−.0309	.0705	−.1258	.1231
2.67	.9962	.0038	.0113	−.0302	.0692	−.1245	.1248
2.68	.9963	.0037	.0110	−.0295	.0680	−.1233	.1264
2.69	.9964	.0036	.0107	−.0288	.0668	−.1220	.1279
2.70	.9965	.0035	.0104	−.0281	.0656	−.1207	.1293
2.71	.9966	.0034	.0101	−.0275	.0644	−.1194	.1306
2.72	.9967	.0033	.0099	−.0269	.0632	−.1181	.1317
2.73	.9968	.0032	.0096	−.0262	.0620	−.1168	.1328
2.74	.9969	.0031	.0093	−.0256	.0608	−.1154	.1338
2.75	.9970	.0030	.0091	−.0250	.0597	−.1141	.1347
2.76	.9971	.0029	.0088	−.0244	.0585	−.1127	.1356
2.77	.9972	.0028	.0086	−.0238	.0574	−.1114	.1363
2.78	.9973	.0027	.0084	−.0233	.0563	−.1100	.1369
2.79	.9974	.0026	.0081	−.0227	.0552	−.1087	.1375
2.80	.9974	.0026	.0079	−.0222	.0541	−.1073	.1379
2.81	.9975	.0025	.0077	−.0216	.0531	−.1059	.1383
2.82	.9976	.0024	.0075	−.0211	.0520	−.1045	.1386
2.83	.9977	.0023	.0073	−.0206	.0510	−.1031	.1389
2.84	.9977	.0023	.0071	−.0201	.0500	−.1017	.1390
2.85	.9978	.0022	.0069	−.0196	.0490	−.1003	.1391
2.86	.9979	.0021	.0067	−.0191	.0480	−.0990	.1391
2.87	.9979	.0021	.0065	−.0186	.0470	−.0976	.1391
2.88	.9980	.0020	.0063	−.0182	.0460	−.0962	.1389
2.89	.9981	.0019	.0061	−.0177	.0451	−.0948	.1388
2.90	.9981	.0019	.0060	−.0173	.0441	−.0934	.1385
2.91	.9982	.0018	.0058	−.0168	.0432	−.0920	.1382
2.92	.9982	.0018	.0056	−.0164	.0423	−.0906	.1378
2.93	.9983	.0017	.0055	−.0160	.0414	−.0893	.1374
2.94	.9984	.0016	.0053	−.0156	.0405	−.0879	.1369
2.95	.9984	.0016	.0051	−.0152	.0396	−.0865	.1364
2.96	.9985	.0015	.0050	−.0148	.0388	−.0852	.1358
2.97	.9985	.0015	.0048	−.0144	.0379	−.0838	.1352
2.98	.9986	.0014	.0047	−.0140	.0371	−.0825	.1345
2.99	.9986	.0014	.0046	−.0137	.0363	−.0811	.1337
3.00	.9987	.0013	.0044	−.0133	.0355	−.0798	.1330

NORMAL DISTRIBUTION AND RELATED FUNCTIONS

x	$F(x)$	$1 - F(x)$	$f(x)$	$f'(x)$	$f''(x)$	$f'''(x)$	$f^{iv}(x)$
3.00	.9987	.0013	.0044	−.0133	.0355	−.0798	.1330
3.01	.9987	.0013	.0043	−.0130	.0347	−.0785	.1321
3.02	.9987	.0013	.0042	−.0126	.0339	−.0771	.1313
3.03	.9988	.0012	.0040	−.0123	.0331	−.0758	.1304
3.04	.9988	.0012	.0039	−.0119	.0324	−.0745	.1294
3.05	.9989	.0011	.0038	−.0116	.0316	−.0732	.1285
3.06	.9989	.0011	.0037	−.0113	.0309	−.0720	.1275
3.07	.9989	.0011	.0036	−.0110	.0302	−.0707	.1264
3.08	.9990	.0010	.0035	−.0107	.0295	−.0694	.1254
3.09	.9990	.0010	.0034	−.0104	.0288	−.0682	.1243
3.10	.9990	.0010	.0033	−.0101	.0281	−.0669	.1231
3.11	.9991	.0009	.0032	−.0099	.0275	−.0657	.1220
3.12	.9991	.0009	.0031	−.0096	.0268	−.0645	.1208
3.13	.9991	.0009	.0030	−.0093	.0262	−.0633	.1196
3.14	.9992	.0008	.0029	−.0091	.0256	−.0621	.1184
3.15	.9992	.0008	.0028	−.0088	.0249	−.0609	.1171
3.16	.9992	.0008	.0027	−.0086	.0243	−.0598	.1159
3.17	.9992	.0008	.0026	−.0083	.0237	−.0586	.1146
3.18	.9993	.0007	.0025	−.0081	.0232	−.0575	.1133
3.19	.9993	.0007	.0025	−.0079	.0226	−.0564	.1120
3.20	.9993	.0007	.0024	−.0076	.0220	−.0552	.1107
3.21	.9993	.0007	.0023	−.0074	.0215	−.0541	.1093
3.22	.9994	.0006	.0022	−.0072	.0210	−.0531	.1080
3.23	.9994	.0006	.0022	−.0070	.0204	−.0520	.1066
3.24	.9994	.0006	.0021	−.0068	.0199	−.0509	.1053
3.25	.9994	.0006	.0020	−.0066	.0194	−.0499	.1039
3.26	.9994	.0006	.0020	−.0064	.0189	−.0488	.1025
3.27	.9995	.0005	.0019	−.0062	.0184	−.0478	.1011
3.28	.9995	.0005	.0018	−.0060	.0180	−.0468	.0997
3.29	.9995	.0005	.0018	−.0059	.0175	−.0458	.0983
3.30	.9995	.0005	.0017	−.0057	.0170	−.0449	.0969
3.31	.9995	.0005	.0017	−.0055	.0166	−.0439	.0955
3.32	.9995	.0005	.0016	−.0054	.0162	−.0429	.0941
3.33	.9996	.0004	.0016	−.0052	.0157	−.0420	.0927
3.34	.9996	.0004	.0015	−.0050	.0153	−.0411	.0913
3.35	.9996	.0004	.0015	−.0049	.0149	−.0402	.0899
3.36	.9996	.0004	.0014	−.0047	.0145	−.0393	.0885
3.37	.9996	.0004	.0014	−.0046	.0141	−.0384	.0871
3.38	.9996	.0004	.0013	−.0045	.0138	−.0376	.0857
3.39	.9997	.0003	.0013	−.0043	.0134	−.0367	.0843
3.40	.9997	.0003	.0012	−.0042	.0130	−.0359	.0829
3.41	.9997	.0003	.0012	−.0041	.0127	−.0350	.0815
3.42	.9997	.0003	.0012	−.0039	.0123	−.0342	.0801
3.43	.9997	.0003	.0011	−.0038	.0120	−.0334	.0788
3.44	.9997	.0003	.0011	−.0037	.0116	−.0327	.0774
3.45	.9997	.0003	.0010	−.0036	.0113	−.0319	.0761
3.46	.9997	.0003	.0010	−.0035	.0110	−.0311	.0747
3.47	.9997	.0003	.0010	−.0034	.0107	−.0304	.0734
3.48	.9997	.0003	.0009	−.0033	.0104	−.0297	.0721
3.49	.9998	.0002	.0009	−.0032	.0101	−.0290	.0707
3.50	.9998	.0002	.0009	−.0031	.0098	−.0283	.0694

NORMAL DISTRIBUTION AND RELATED FUNCTIONS

x	$F(x)$	$1 - F(x)$	$f(x)$	$f'(x)$	$f''(x)$	$f'''(x)$	$f^{iv}(x)$
3.50	.9998	.0002	.0009	−.0031	.0098	−.0283	.0694
3.51	.9998	.0002	.0008	−.0030	.0095	−.0276	.0681
3.52	.9998	.0002	.0008	−.0029	.0093	−.0269	.0669
3.53	.9998	.0002	.0008	−.0028	.0090	−.0262	.0656
3.54	.9998	.0002	.0008	−.0027	.0087	−.0256	.0643
3.55	.9998	.0002	.0007	−.0026	.0085	−.0249	.0631
3.56	.9998	.0002	.0007	−.0025	.0082	−.0243	.0618
3.57	.9998	.0002	.0007	−.0024	.0080	−.0237	.0606
3.58	.9998	.0002	.0007	−.0024	.0078	−.0231	.0594
3.59	.9998	.0002	.0006	−.0023	.0075	−.0225	.0582
3.60	.9998	.0002	.0006	−.0022	.0073	−.0219	.0570
3.61	.9998	.0002	.0006	−.0021	.0071	−.0214	.0559
3.62	.9999	.0001	.0006	−.0021	.0069	−.0208	.0547
3.63	.9999	.0001	.0005	−.0020	.0067	−.0203	.0536
3.64	.9999	.0001	.0005	−.0019	.0065	−.0198	.0524
3.65	.9999	.0001	.0005	−.0019	.0063	−.0192	.0513
3.66	.9999	.0001	.0005	−.0018	.0061	−.0187	.0502
3.67	.9999	.0001	.0005	−.0017	.0059	−.0182	.0492
3.68	.9999	.0001	.0005	−.0017	.0057	−.0177	.0481
3.69	.9999	.0001	.0004	−.0016	.0056	−.0173	.0470
3.70	.9999	.0001	.0004	−.0016	.0054	−.0168	.0460
3.71	.9999	.0001	.0004	−.0015	.0052	−.0164	.0450
3.72	.9999	.0001	.0004	−.0015	.0051	−.0159	.0440
3.73	.9999	.0001	.0004	−.0014	.0049	−.0155	.0430
3.74	.9999	.0001	.0004	−.0014	.0048	−.0150	.0420
3.75	.9999	.0001	.0004	−.0013	.0046	−.0146	.0410
3.76	.9999	.0001	.0003	−.0013	.0045	−.0142	.0401
3.77	.9999	.0001	.0003	−.0012	.0043	−.0138	.0392
3.78	.9999	.0001	.0003	−.0012	.0042	−.0134	.0382
3.79	.9999	.0001	.0003	−.0012	.0041	−.0131	.0373
3.80	.9999	.0001	.0003	−.0011	.0039	−.0127	.0365
3.81	.9999	.0001	.0003	−.0011	.0038	−.0123	.0356
3.82	.9999	.0001	.0003	−.0010	.0037	−.0120	.0347
3.83	.9999	.0001	.0003	−.0010	.0036	−.0116	.0339
3.84	.9999	.0001	.0003	−.0010	.0034	−.0113	.0331
3.85	.9999	.0001	.0002	−.0009	.0033	−.0110	.0323
3.86	.9999	.0001	.0002	−.0009	.0032	−.0107	.0315
3.87	.9999	.0001	.0002	−.0009	.0031	−.0104	.0307
3.88	.9999	.0001	.0002	−.0008	.0030	−.0100	.0299
3.89	1.0000	.0000	.0002	−.0008	.0029	−.0098	.0292
3.90	1.0000	.0000	.0002	−.0008	.0028	−.0095	.0284
3.91	1.0000	.0000	.0002	−.0008	.0027	−.0092	.0277
3.92	1.0000	.0000	.0002	−.0007	.0026	−.0089	.0270
3.93	1.0000	.0000	.0002	−.0007	.0026	−.0086	.0263
3.94	1.0000	.0000	.0002	−.0007	.0025	−.0084	.0256
3.95	1.0000	.0000	.0002	−.0006	.0024	−.0081	.0250
3.96	1.0000	.0000	.0002	−.0006	.0023	−.0079	.0243
3.97	1.0000	.0000	.0002	−.0006	.0022	−.0076	.0237
3.98	1.0000	.0000	.0001	−.0006	.0022	−.0074	.0230
3.99	1.0000	.0000	.0001	−.0006	.0021	−.0072	.0224
4.00	1.0000	.0000	.0001	−.0005	.0020	−.0070	.0218

x	1.282	1.645	1.960	2.326	2.576	3.090
$F(x)$	.90	.95	.975	.99	.995	.999
$2[1 - F(x)]$	.20	.10	.05	.02	.01	.002

Polynomial approximations for $\Gamma(x)$

Abramowitz and Stegun p. 257

for $0 \leq x \leq 1$

$$\Gamma(x+1) = x\Gamma(x)$$
$$= 1 + b_1 x + \cdots + b_8 x^8 + \varepsilon(x)$$
$$|\varepsilon(x)| \leq 3 \times 10^{-7}$$

$b_1 = -0.577191652$
$b_2 = 0.988205891$
$b_3 = -0.897056937$
$b_4 = 0.918206857$
$b_5 = -0.756704078$
$b_6 = 0.482199394$
$b_7 = -0.193527818$
$b_8 = 0.035868343$

Test values

$\Gamma(\frac{1}{4}) = 3.6256099082$
$\Gamma(\frac{1}{3}) = 2.6789385347$
$\Gamma(\frac{1}{2}) = \sqrt{\pi}$
$\Gamma(\frac{2}{3}) = 1.3541179394$
$\Gamma(\frac{3}{4}) = 1.2254167024$

$\Gamma(\frac{3}{4}) = -\frac{1}{4}\Gamma(-\frac{1}{4})$

$\Gamma(n+1) = n!$

$\Gamma(3.75) \doteq$
$\Gamma(1.75) = 0.75\,\Gamma(0.75)$
$\Gamma(2.75) = \Gamma(1.75+1) = 1.75 \times 0.75\,\Gamma(0.75)$
$\Gamma(3.75) = \Gamma(2.75+1) = 2.75 \times 1.75 \times 0.75\,\Gamma(0.75)$

$$\frac{2^{3/2}}{4 \cdot 1!}\Gamma\left(\frac{1}{4}\right)$$

Evaluation of the Incomplete Gamma Function

$$P(a,x) = \frac{1}{\Gamma(a)}\int_0^x e^{-t}t^{a-1}\,dt = \frac{\gamma(a,x)}{\Gamma(a)}$$

$$\therefore \gamma^*(a,x) = x^{-a}P(a,x) \qquad \therefore P(a,x) = x^a\gamma^*(a,x)$$

Series development for $\gamma^*(a,z)$

$$\gamma^*(a,z) = e^{-z}\sum_{n=0}^{\infty}\frac{z^n}{\Gamma(a+n+1)} = e^{-z}\left[\frac{1}{a\Gamma(a)} + \frac{z}{(a+1)a\Gamma(a)} + \cdots\right.$$

$$= \frac{1}{\Gamma(a)}\sum_{n=0}^{\infty}\frac{(-z)^n}{(a+n)\,n!}$$

$$n=0 \qquad \frac{1}{\Gamma(a+1)} = \frac{1}{a\Gamma(a)}$$

$$n=1 \qquad \frac{z}{\Gamma(a+2)} = \frac{z}{(a+1)a\Gamma(a)}$$

$$n=2 \qquad \frac{z^2}{\Gamma(a+3)} = \frac{z^2}{(a+2)(a+1)a\Gamma(a)}$$

$$\gamma^*(a,z) = \frac{e^{-z}}{a\Gamma(a)}\left[1 + \frac{z}{a+1} + \frac{z^2}{(a+2)(a+1)} + \cdots\right]$$

For the energy distribution $P(E>E_0) = \frac{2}{\sqrt{\pi}}\int_{E_0/kT}^{\infty}u^{\frac12}e^{-u}\,du$

$$= \frac{2}{\sqrt{\pi}}\left[\Gamma\left(\tfrac32\right) - \gamma\left(\tfrac32, \tfrac{E_0}{kT}\right)\right] = 1 - \frac{\gamma\left(\frac32, \frac{E_0}{kT}\right)}{\Gamma\left(\frac32\right)} = 1 - P\left(\tfrac32, \tfrac{E_0}{kT}\right)$$

Test: Calculate $\dfrac{\int_0^{0.9} t^{3/2}e^{-t}\,dt}{\Gamma\left(\frac52\right)} = 1 - 0.87607$

Integral $= \Gamma\left(\frac52\right) P_{\chi^2}(1.8|5)$

$$Q(\chi^2|3)$$

$$\Gamma\left(\tfrac52\right) = \tfrac32\cdot\Gamma\left(\tfrac32\right) = \tfrac32\cdot\tfrac{\sqrt{\pi}}{2} = \tfrac34\sqrt{\pi}$$

Important Questions regarding general approach.

1. Did you find the identification of main mathematical ideas (statistical independence, distribution functions, probability densities, expectation values etc) to be extensive enough? If not, what concepts do you think could have also been included?

3. ~~Was~~ The approach involved ~~use of the~~ introducing the mathematical concepts by use of the functions that subsequently arise in the consideration of specific molecular systems. Did you find this to be a useful way of separating the physical implications of these models from the analytical details?

2. In published textbooks on statistical thermodynamics, is it generally easy or difficult to gain a physical understanding of the systems considered given the mathematical manipulations involved?

4. In introducing each lecture, the approach used involved asking questions to focus attention on
(i) identifying the relevant physical quantities required to describe the system
(ii) What sort of behaviour ~~would~~ one would expect of the systems on intuitive grounds?

Which of these aspects did you consider to be more important to your subsequent understanding?

5. Did you find that the comparison ~~between~~ of your initial expectations of the physical behaviour with
(i) experiment
(ii) the theoretical models
leads to an increase in your understanding?

6. What are the usual characteristics of published textbooks on statistical mechanics? ~~do you~~

6.or: Do you find that ~~certa~~ textbooks on this subject have certain common features? If the answer is 'yes' ~~descri~~ identify these.

7. Can you identify which of these general characteristics promote or impede development of an understanding of the subject?

8. How important do you find numerical examples as an aid to the development of understanding?

Other ideas

1. Include a brief discussion of the epistemological character of the subject. ~~Identify the~~ (e.g., inductive vs hypothetico-deductive) and its relation to observable quantities.
2. Identify the cognitive processes involved
   - — recall of formulae (specific or general?)
   - — input of physical data (check for consistency of units, for example ~~sensible orders of magnitude~~)
   - — analytical manipulations (evaluation of integrals, special functions etc)