CHAPTER 3

SYSTEMS OF A SINGLE COMPONENT

§3.01 *Single components and single phases*

The present chapter is devoted to single component systems, both single phase and multiphase. Most of the formulae of the present chapter which relate to a single closed phase are applicable also to a multicomponent closed phase. Formulae relating to an open phase or to a multiphase system are on the contrary more complicated in a multicomponent system than in a single component system. Such formulae will be derived in chapter 4.

§3.02 *Dependence of entropy on temperature*

The experimental determination of entropy and thermodynamic temperature are interlinked. We have not yet described how either can be directly or conveniently measured. In §3.12 we shall describe an especially convenient way of measuring thermodynamic temperature. Anticipating this result, that is to say assuming we have a thermometer which measures thermodynamic temperature, we shall now describe how we can determine the dependence of entropy on temperature at constant pressure.

For a single closed phase, we have according to (1.28.8)

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P \qquad 3.02.1$$

or if we keep the pressure constant

$$\mathrm{d}H = T\mathrm{d}S \qquad (P \text{ const.}). \qquad 3.02.2$$

If then we supply heat q to a single component system, since the change in the system must be reversible, regardless of whether the process of supplying the heat is reversible (see §1.13), we have

$$q = \mathrm{d}H = T\mathrm{d}S \qquad (P \text{ const.}). \qquad 3.02.3$$

Furthermore if we supply the heat by means of an electric element, the heat will be equal to the electrical work done on the element. To be precise, if the potential difference across the element is E and the current flowing is i, then in a time t the heat given up by the element to the system is Eit. Since E, i, and t are all measurable we can calculate q. We see then that, apart from experimental difficulties, there is no difficulty in principle in measuring increases of H. As already mentioned we are postulating, in anticipation of §3.12, the availability of a thermometer which measures T. We thus obtain a direct experimental relationship between T and H, or rather changes in H which itself contains an arbitrary additive constant.

As an illustration we show in figure 3.1 the experimental data* for one mole of H_2O at a constant pressure of one atmosphere. The first curve on the left applies to ice from 0 K to 273.15 K, at which temperature the ice

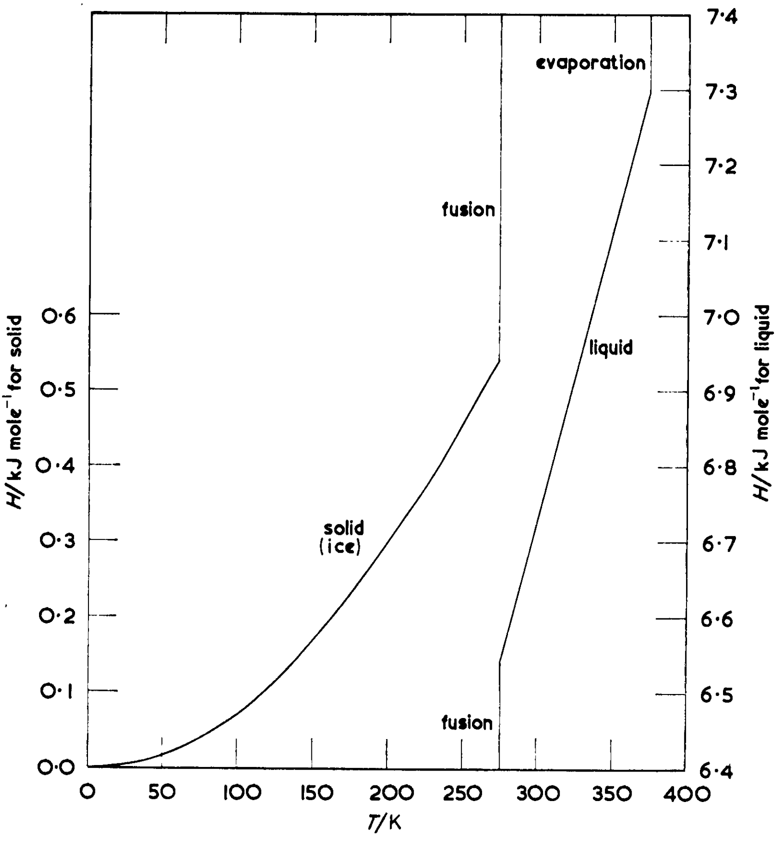

Fig. 3.1. Enthalpy of one mole of H_2O at one atmosphere

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* Giauque and Stout, J. Amer. Chem. Soc. 1936 **58** 1144.

melts; the value of the enthalpy then rises at constant temperature by an amount equal to the *proper enthalpy of fusion.* As this change would run off the paper the scale of the curve for the liquid has been shifted downwards by 6.4 kJ mole^{-1}. The curve on the right of the figure runs from 273.15 K to 373.15 K at which temperature the water boils; the value of the enthalpy again rises at constant temperature and runs off the diagram.

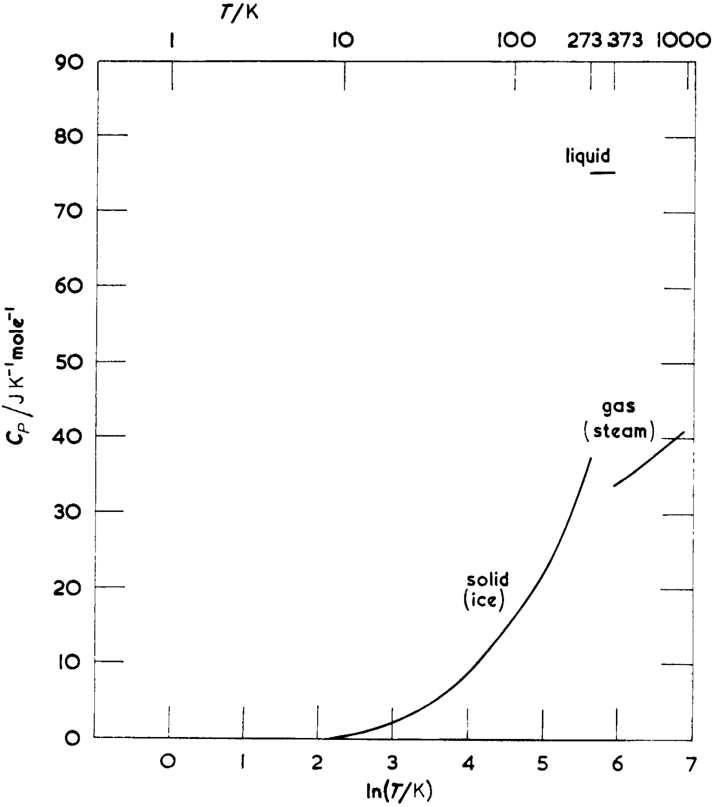

Fig. 3.2. Heat capacity of H_2O at one atmoshpere

In figure 3.2 we show the data in a somewhat different form, $(\partial H/\partial T)_P$ for unit amount or $(\partial H_m/\partial T)_P$ being now plotted against ln T. The three separate curves apply to ice, liquid water, and steam respectively. From (2) we have

$$S_m = \int dS_m = \int dH_m/T = \int (\partial H_m/\partial T)_P \, d\ln T. \qquad 3.02.4$$

We see then that apart from an arbitrary constant the proper entropy of ice at a temperature T is equal to the area under the part of the curve to the left of T. In particular the proper entropy of ice at the fusion point exceeds that at 0 K by an amount corresponding to the whole area under the ice curve. This amounts to 38.09 J K^{-1} mole^{-1}.

When the ice changes to liquid water there is an increase of the proper entropy called the *proper entropy of fusion* equal to the *proper enthalpy of fusion* divided by the temperature. Thus

$$\Delta S_{\mathrm{m}}=\Delta H_{\mathrm{m}}/T=6007 \text{ J mole}^{-1}/273.15 \text{ K}=21.99 \text{ J K}^{-1} \text{ mole}^{-1}.$$

Suppose we wish to know by how much the proper entropy of steam at 1000 K and 1 atm exceeds the proper entropy of ice at 0 K. We have to sum the following contributions.

(a) Ice at 0 K→ice at 273.15 K
$\Delta S_{\mathrm{m}}=38.09 \text{ J K}^{-1} \text{ mole}^{-1}$ (area under ice curve).

(b) Ice at 273.15 K→liquid water at 273.15 K
$\Delta S_{\mathrm{m}}=\Delta H_{\mathrm{m}}/T=6007 \text{ J mole}^{-1}/273.15 \text{ K}=21.99 \text{ J K}^{-1} \text{ mole}^{-1}$.

(c) Water at 273.15 K→water at 373.15 K
$\Delta S_{\mathrm{m}}=23.52 \text{ J K}^{-1} \text{ mole}^{-1}$ (area under water curve).

(d) Water at 373.15 K→steam at 373.15 K
$\Delta S_{\mathrm{m}}=\Delta H_{\mathrm{m}}/T=40656 \text{ J mole}^{-1}/373.15 \text{ K}=108.95 \text{ J K}^{-1} \text{ mole}^{-1}$.

(e) Steam at 373.15 K→steam at 1000 K
$\Delta S_{\mathrm{m}}=35.8 \text{ J K}^{-1} \text{ mole}^{-1}$ (area under steam curve).

By addition we obtain for the change
Ice at 0 K→steam at 1000 K (at 1 atm)
$\Delta S_{\mathrm{m}}=228.4 \text{ J K}^{-1} \text{ mole}^{-1}$.

In the case of some substances there may be several solid phases with transition temperatures at which the proper entropy increase ΔS_{m} is equal to the increase ΔH_{m} divided by T. Such transitions cause no difficulty.

We see then that the determination of changes in the entropy of any single substance through any range of temperature at constant pressure becomes straightforward provided the heat input and thermodynamic temperature can be measured.

§3.03 *Heat capacity at constant pressure*

In the previous section we saw that the determination of entropy requires us to use the relation

$$T(\partial S/\partial T)_P=(\partial H/\partial T)_P. \qquad 3.03.1$$

This quantity is called the *heat capacity at constant pressure* of the system.

The heat capacity per unit amount or the *proper heat capacity at constant pressure* will be denoted by C, or by C_P when it is desired to emphasize the contrast with another quantity C_V defined in §3.06. Thus

$$C = C_P = T(\partial S_m/\partial T)_P = (\partial H_m/\partial T)_P. \qquad 3.03.2$$

The importance of C is that it forms the connecting link between S and H. One measures directly H as a function of T and then determines S by the relation (1). Importance was in the past attached to C for a completely different, accidental, and inadequate reason, namely that for many substances at the most usual temperatures C happens to be insensitive to the temperature. For example we notice from figure 3.2 that C is nearly constant for liquid water, only roughly constant for steam, but not at all constant for ice.

The heat capacity at constant pressure per unit mass or the *specific heat capacity at constant pressure* is denoted by c_P.

§3.04 *So-called mechanical equivalent of heat*

Before the classical experiments of Joule, the relationship between work, heat, and energy was not understood. These experiments established that within the experimental error the work or energy input required to raise the temperature of a given mass of water through a given temperature range is independent of the particular mechanism used. The formulation of the first law of thermodynamics is largely based on these experiments and later repetitions and improvements of them. Since Joule's experiments were performed before the formulation of the first law, Joule's terminology was necessarily different from the terminology based on familiarity with the laws of thermodynamics. Joule described some of his experiments as the 'determination of the mechanical equivalent of heat'. Once the principles of thermodynamics are understood, this phrase becomes meaningless. What Joule in fact did was

(a) to establish an experimental basis for the formulation of the first law of thermodynamics;

(b) to measure the heat capacity of water.

Before the first law of thermodynamics was formulated or understood the unit of heat was the quantity of heat required to raise the temperature of one gramme of water by one degree and this unit was called the calorie. Work was however measured in mechanical units. It is found that the specific heat capacity of liquid water is approximately 4.18 J $K^{-1}g^{-1}$ but in fact varies appreciably with the temperature. Nowadays almost all accurate thermal experiments involve measurements of volts, amperes, and seconds leading to energy values in joules. Moreover in 1948 the Conférence Générale des Poids et Mesures adopted* a recommendation of the International Union of Pure and Applied Physics that all accurate calorimetric data should be expressed in joules. It is difficult to understand why the use of the calorie as a unit persists, except as a habit. The most careful experimental workers in thermochemistry have abandoned the old definition of the calorie and have replaced it by the more satisfactory definition

$$1 \text{ calorie} = 4.184 \text{ joules exactly.}$$

The calorie thus defined is called the *thermochemical calorie.*

As already mentioned the specific heat capacity of liquid water is approximately, but by no means exactly, independent of the temperature. Its value is very near 1 cal $K^{-1}g^{-1}$ at 290 K. The best experimental values at a few other temperatures are as follows†:

At	0 °C	4.2174 J $K^{-1}g^{-1}$
	15 °C	4.1855 J $K^{-1}g^{-1}$
	16 °C	4.1846 J $K^{-1}g^{-1}$
	17 °C	4.1837 J $K^{-1}g^{-1}$
	20 °C	4.1816 J $K^{-1}g^{-1}$
	25 °C	4.1793 J $K^{-1}g^{-1}$.

§3.05 *Dependence of entropy on pressure*

In §3.02 we saw how the variation of entropy with the temperature at a constant pressure is determined experimentally. In order to determine the entropy as a function of temperature and pressure, this procedure has to be supplemented by a determination of the dependence of entropy on pressure at constant temperature. This dependence is given according to Maxwell's relation (1.48.2)

$$(\partial S_{\mathrm{m}}/\partial P)_T = -\alpha V_{\mathrm{m}} \qquad 3.05.1$$

which when integrated becomes

$$S_{\mathrm{m}}(T, P_2) - S_{\mathrm{m}}(T, P_1) = -\int_{P_1}^{P_2} \alpha V_{\mathrm{m}} \, \mathrm{d}P. \qquad 3.05.2$$

If we differentiate (1) with respect to T, keeping P constant, and multiply by

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* C.R. Conférence Générale des Poids et Mesures 1948.

† Stille, Messen und Rechnen in der Physik, Vieweg 1955, p. 289.

T we obtain

$$(\partial C/\partial P)_T = -T\{\partial(\alpha V_\mathrm{m})/\partial T\}_P = -\alpha^2 T V_\mathrm{m} - T(\partial\alpha/\partial T)_P V_\mathrm{m}. \qquad 3.05.3$$

For solids and liquids the second term on the right may be small compared with the first; for gases on the contrary the two terms are nearly equal and opposite.

§3.06 *Heat capacity at constant volume*

In §§3.02–3.05 we have collected the most important formulae required to determine the entropy in terms of temperature and pressure. There is an analogous set of relations for the alternative choice of temperature and volume as independent variables. Except for gases these relations are considerably less useful than those relating to the independent variables T, P. We shall refer to them briefly, without giving detailed derivations; these are in all cases analogous to those in the T, P system.

For the dependence of entropy on temperature at constant volume, we have

$$(\partial S/\partial T)_V = T^{-1}(\partial U/\partial T)_V \qquad 3.06.1$$

which when integrated becomes

$$S(T_2, V) - S(T_1, V) = \int_{T_1}^{T_2} (\partial U/\partial T)_V \,\mathrm{d}\ln T. \qquad 3.06.2$$

Correspondingly for the dependence of entropy on volume at constant temperature, we have according to Maxwell's relation (1.47.3)

$$(\partial S/\partial V)_T = \alpha/\kappa_T \qquad 3.06.3$$

which when integrated becomes

$$S(T, V_2) - S(T, V_1) = \int_{V_1}^{V_2} (\alpha/\kappa_T)\mathrm{d}V. \qquad 3.06.4$$

The quantity $(\partial U/\partial T)_V$ in formula (1) is called the *heat capacity at constant volume* of the system. The corresponding quantity referred to unit amount, the *proper heat capacity at constant volume*, is denoted by C_V. Thus

$$C_V = T(\partial S_\mathrm{m}/\partial T)_V = (\partial U_\mathrm{m}/\partial T)_V. \qquad 3.06.5$$

The heat capacity at constant volume per unit mass or the *specific heat capacity at constant volume* is denoted by c_V.

§3.07 *Relation between heat capacities*

According to the meaning of partial differential coefficients we have

$$(\partial S/\partial T)_P=(\partial S/\partial T)_V+(\partial S/\partial V)_T(\partial V/\partial T)_P. \qquad 3.07.1$$

Substituting from (1.46.2), (1.46.3), and from Maxwell's relation (1.47.3) into (1) we obtain

$$(\partial S/\partial T)_P=(\partial S/\partial T)_V+\alpha^2 V/\kappa_T. \qquad 3.07.2$$

Applying (2) to unit quantity, multiplying by T, and using the definitions (3.03.2) and (3.06.5) of C_P and C_V respectively we find

$$C_P=C_V+\alpha^2 TV_\mathrm{m}/\kappa_T. \qquad 3.07.3$$

Since in a stable phase none of the quantities α^2, T, V_m, κ_T can ever be negative, it follows that C_P can never be less than C_V.

C_V is much more difficult to measure than C_P. If the value of C_V is required, it is usual to measure C_P and then calculate C_V from (3). There seems to be a widespread belief that in the comparison of a theoretical model with experimental data the most suitable quantity for the comparison is C_V. This is however a misconception. Any theoretical model susceptible to explicit analytical treatment, such as for example Debye's model of a crystal discussed in §3.33, leads to an explicit formula for the Helmholtz function and so by differentiation with respect to T to explicit formulae for the energy and the entropy, both of which are directly measurable as a function of temperature. These are clearly the most suitable quantities for comparison between a theoretical model of a crystal and experimental data. There is no reason or excuse for a further differentiation to obtain a heat capacity except in the hypothetical case that the agreement between theory and experiment is so good that a more sensitive test is required.

§3.08 *Adiabatic compressibility*

In §1.46 the isothermal compressibility κ_T was defined by

$$\kappa_T=-V^{-1}(\partial V/\partial P)_T. \qquad 3.08.1$$

The adiabatic compressibility κ_S is similarly defined by

$$\kappa_S=-V^{-1}(\partial V/\partial P)_S. \qquad 3.08.2$$

These two compressibilities are interrelated as follows.

$$\frac{\kappa_S}{\kappa_T}=\frac{(\partial V/\partial P)_S}{(\partial V/\partial P)_T}=\frac{(\partial S/\partial P)_V(\partial P/\partial T)_V}{(\partial S/\partial V)_P(\partial V/\partial T)_P}=\frac{(\partial S/\partial T)_V}{(\partial S/\partial T)_P}=\frac{C_V}{C_P}. \qquad 3.08.3$$

The speed a of propagation of compressional sound waves in an isotropic medium is given by

$$a^2 = V_m/M\kappa_S \qquad 3.08.4$$

where M is the proper mass. From (3), (4), and (3.07.3) we deduce

$$C_P/C_V - 1 = \alpha^2 TMa^2/C_P. \qquad 3.08.5$$

This is the most useful formula for determining C_P/C_V since all the quantities on the right, in contrast to C_V, and in solids κ_T, are readily measurable.

§3.09 *Condensed phases and gases*

Solids and liquids, which we shall class together under the name *condensed phases*, are under most conditions sharply distinguished from gases by a striking difference in compressibility. It is true that in the neighbourhood of the critical point, as we shall see in §3.44 the distinction between liquid and gas disappears, but at least for liquids or solids at temperatures well below the critical temperature and for gases at pressures well below the critical pressure the contrast is striking.

In a condensed phase at a given temperature the compressibility is small and practically independent of the pressure. That is to say that to a first approximation the volume is independent of the pressure and to a better approximation decreases linearly with the pressure. In a gas on the other hand the compressibility is much greater and far from independent of the pressure. In fact it is at least roughly true that the volume of a gas varies inversely as the pressure, according to Boyle's Law. In other words it is PV, not V, which to a first approximation is independent of P.

§3.10 *Isothermal behaviour of a gas*

It is reasonable to expect that the volume of any phase at constant temperature can be expressed as a power series in the density or the reciprocal of the proper volume. In view of what was said in the previous section, the leading term will in the case of a gas be an inverse first power. We may accordingly write

$$PV_m = A(1 + B_2/V_m + B_3/V_m^2 + B_4/V_m^3 + \ldots). \qquad 3.10.1$$

In principle the number of terms is indefinite, depending on the accuracy aimed at. Up to quite high pressures, of say a hundred atmospheres, it is often unnecessary to use more than three terms. At pressures up to a few atmospheres even the third term is often negligible, only the first two terms being required.

All the coefficients A, B_2, B_3, ... of course depend on the temperature, but not on the volume.

B_2 is called* the second virial coefficient; B_3 is called the third virial coefficient and so on.

For the sake of simplicity and brevity we shall replace (1) by the three term expression

$$PV_\mathrm{m}=A(1+B_2/V_\mathrm{m}+B_3/V_\mathrm{m}^2). \qquad 3.10.2$$

There is in principle no difficulty in inserting further terms if required.

We can invert the series in (2) to obtain the expansion in powers of P

$$PV_\mathrm{m}=A+B_2P+A^{-1}(B_3-B_2^2)P^2+\dots. \qquad 3.10.3$$

It is mainly a question of convenience whether one uses a formula of type (2) or of type (3). For our immediate purpose, it is more convenient to use (3). Fortunately at ordinary pressures all terms beyond the second are usually negligible and either formula then reduces to

$$V=A/P+B_2 \qquad \text{(low pressures).} \qquad 3.10.4$$

From (3) we readily obtain the proper Gibbs function G_m as a function of pressure by substituting into (3) and integrating. We thus find

$$G_\mathrm{m}(T,P)-G_\mathrm{m}(T,P^\ominus)=A\ln(P/P^\ominus)+B_2(P-P^\ominus)+\tfrac{1}{2}A^{-1}(B_3-B_2^2)(P^2-P^{\ominus 2}) \qquad 3.10.5$$

where $P^\ominus$ is a standard pressure, which may be chosen arbitrarily, but in this book is always 1 atm. This does not imply that pressures must necessarily be measured in atm. In other units we have for example

$$P^\ominus=1\ \mathrm{atm}=76\ \mathrm{cmHg}=760\ \mathrm{mmHg}=$$
$$=1.01325\times10^6\ \mathrm{dyn\ cm^{-2}}=1.01325\times10^5\ \mathrm{J\ m^{-3}}=1.01325\ \mathrm{bar}.$$

We obtain for the proper enthalpy H_m by substituting (5) into (1.49.3)

$$\begin{aligned}H_\mathrm{m}(T,P)-H_\mathrm{m}(T,P^\ominus)=&\{\mathrm{d}(T^{-1}A)/\mathrm{d}T^{-1}\}\ln(P/P^\ominus)\\&+\{\mathrm{d}(T^{-1}B_2)/\mathrm{d}T^{-1}\}(P-P^\ominus)\\&+\tfrac{1}{2}\{\mathrm{d}(T^{-1}A^{-1}B_3-T^{-1}A^{-1}B_2^2)/\mathrm{d}T^{-1}\}(P^2-P^{\ominus 2}).\end{aligned} \qquad 3.10.6$$

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[*] Onnes and Keesom, 'Die Zustandsgleichung'. Commun. Phys. Lab. Univ. Leiden, 11: Suppl. 23 1912; Encyk. Math. Wiss., 5: No. 10, p. 615.

§3.11 *Throttling*

In the previous section we set up a formula for V_m as a function of P based on experiment. From this we deduced a formula for G_m and thence a formula for H_m. We shall now consider the comparison between this formula for H_m and experiment.

The experiment which supplies the most direct information concerning the dependence of H on the pressure at constant temperature is known as *throttling*. The first experiment of this type was performed by Joule and Lord Kelvin (William Thomson); it is accordingly often called the *Joule–Thomson experiment*. In this experiment a stream of gas in a thermally insulated container is forced through a plug, the pressure being greater on the near side than on the far side and the temperatures of the gas stream approaching and leaving the plug are measured on an arbitrary scale; we denote the temperatures on this scale by θ to distinguish them sharply from thermodynamic temperatures T, which we do not yet know how to measure. Consider now the whole system in a steady state such that in a given time a certain mass of gas is pushed in at a pressure P_1 and during the same time an equal mass of gas streams away at a pressure P_2. We use the subscript 1 to denote the state of the gas being pushed in and the subscript 2 to denote that of the gas streaming away. Then during the time considered a mass of gas of pressure P_2, volume V_2, temperature θ_2, and energy U_2 is displaced by an equal mass of pressure P_1, volume V_1, temperature θ_1, and energy U_1. During this time the work done on the system is $P_1V_1-P_2V_2$. Since the system is supposed thermally insulated this work must be equal to the increase in energy of the system. Thus

$$U_2-U_1=P_1V_1-P_2V_2. \qquad 3.11.1$$

Hence according to the definition of H in §1.28, we have

$$H_2=H_1 \qquad 3.11.2$$

or choosing θ, P as independent variables

$$H(\theta_1,P_1)=H(\theta_2,P_2). \qquad 3.11.3$$

Suppose that the effect of throttling is to cool the gas, so that θ_2 is a lower temperature than θ_1, then there is no difficulty in principle in heating the throttled gas at constant pressure so as to restore its temperature from θ_2 to θ_1. If the heat required for this purpose is measured, we then know the value of

$$H(\theta_1,P_2)-H(\theta_2,P_2) \qquad 3.11.4$$

which according to (3) is equal to

$$H(\theta_1, P_2) - H(\theta_1, P_1). \qquad 3.11.5$$

If on the contrary the effect of throttling is to warm the gas, then one must do a subsidiary experiment to determine the heat required to raise the temperature of the gas at the pressure P_2 from θ_1 to θ_2. We thus obtain an experimental value of

$$H(\theta_2, P_2) - H(\theta_1, P_2) \qquad 3.11.6$$

which according to (3) is equal to

$$H(\theta_1, P_1) - H(\theta_1, P_2). \qquad 3.11.7$$

In either case we obtain experimental values of $H(\theta_1, P_2) - H(\theta_1, P_1)$ positive in the former case, negative in the latter. It is important to notice that this experiment does not require any knowledge of how the arbitrary θ scale of temperature is related to the thermodynamic scale or to any other scale.

We shall now describe the experimental results obtained. It is found that, whatever the temperature, $H(P_1) - H(P_2)$ is at least approximately proportional to $P_1 - P_2$ and is not sensitive to the absolute magnitude of P_1. It is quite certain that at low values of P_2, the value of $H(P_1) - H(P_2)$ does not tend towards infinity, which is what one should expect from formula (3.10.6) owing to the term in $\ln P$. In short the Joule–Thomson experiment shows that the first term on the right of formula (3.10.6) is in fact missing and the linear term in P is therefore the leading one.

§3.12 *Measurement of thermodynamic temperature*

In principle to determine T, one should measure ΔH and ΔG for the same isothermal process and by comparing these obtain a differential equation for T. In particular, one can determine the coefficients A, B_2, B_3, in the formula for G simply by pressure measurements and one can obtain independent measurements of the corresponding coefficients in H, from the throttling experiment. By comparison we obtain information concerning T, but admittedly in a rather awkward form.

To our agreeable surprise the information is in a strikingly convenient form in the case of the coefficient A. The throttling experiment shows unmistakably that H contains no term tending to infinity as P tends to zero, that is to say no term in $\ln P$. Hence from (3.10.6) we conclude that

$$\mathrm{d}(T^{-1}A)/\mathrm{d}T^{-1} = 0 \qquad 3.12.1$$

which is equivalent to

$$A \propto T. \qquad 3.12.2$$

At last we have found a simple, direct, and reliable way of determining the ratio of any two thermodynamic temperatures. We use as a thermometer a fixed quantity of gas. We measure several pairs of values of P, V at the same temperature and extrapolate the product PV to $P=0$, thus obtaining the value of A. We repeat this at another temperature thus obtaining another value of A. Then the ratio of these two values of A is equal to the ratio of the two values of T. Having thus established a way of determining the ratio of any two temperatures, the numerical values are fixed by the convention described in §1.21 so that the triple point of water is 273.16 degrees Kelvin and this is called the Kelvin scale.

§3.13 *The gas constant and the mole*

We have found that the coefficient A is directly proportional to the temperature. We accordingly write

$$A = RT \qquad 3.13.1$$

where R is independent of temperature and pressure. R also becomes independent of the nature of the gas when the unit of amount is suitably chosen, e.g. by choosing the mole. From a purely thermodynamic view-point the amount of substance may be defined without any reference to molecular theory by assigning a common value of R to all gaseous substances.

The accepted definition* of the *mole* is that amount of substance which contains the same number of molecules as there are atoms in 0.012 kg of ^{12}C. In this definition 'molecules' includes ions, radicals, electrons, etc. The number of atoms in 0.012 kg of ^{12}C is 0.60225×10^{24}. Consequently the factor for transforming moles to molecules, called *the Avogadro constant L*, is

$$L = 0.60225 \times 10^{24} \text{ mole}^{-1}$$

and the factor for converting molecules to moles is

$$L^{-1} = 1.66044 \times 10^{-24} \text{ mole.}$$

It can be shown by statistical mechanics or kinetic theory that the gas constant has a common value for all gases and is related to the Boltzmann constant k introduced in chapter 2 by

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* I.U.P.A.P. Symbols, Units and Nomenclature in Physics, 1961 p. 19, 1965 p. 25; I.U.P.A.C. Information Bulletin Number 24 1965 p. 4.

$$\begin{aligned} R &= Lk \\ &= 6.0225\times 10^{24}\ \text{mole}^{-1}\times 1.3805\times 10^{-23}\ \text{J K}^{-1} \\ &= 8.3143\ \text{J K}^{-1}\ \text{mole}^{-1}. \end{aligned}$$

§3.14 *Isothermal equation of a gas*

When we replace A by RT in (3.10.2) we obtain

$$PV_{\mathrm{m}}/RT = 1 + B_2/V_{\mathrm{m}} + B_3/V_{\mathrm{m}}^2. \qquad 3.14.1$$

It is convenient to call PV_{m}/RT the *compression factor*. It is sometimes denoted by Z. When the density is sufficiently low for B_2/V_{m}, and a fortiori B_3/V_{m}^2, to be negligible the gas is called a *perfect gas.*

§3.15 *Absolute activity*

In chapter 2 we met a quantity called the *absolute activity* which plays an important part in the statistical thermodynamics of open systems. We now give a purely thermodynamic definition of the absolute activity. This is somewhat out of place in the present chapter, but we could not give it earlier because it involves the gas constant R. We accordingly define* the absolute activity as related to the molar chemical potential μ by

$$\lambda = \exp(\mu/RT) \qquad 3.15.1$$

or

$$\mu = RT \ln \lambda. \qquad 3.15.2$$

Whereas it is not necessary to use λ as well as μ, we shall find that the absolute activity λ is often a convenient function in the study of equilibria of all kinds whether involving one species or several. In § 1.44 we showed that for the most general chemical reaction represented symbolically by

$$0 = \sum_{\mathrm{B}} \nu_{\mathrm{B}} \mathrm{B} \qquad 3.15.3$$

the condition for equilibrium is according to (1.44.13)

$$\sum_{\mathrm{B}} \nu_{\mathrm{B}} \mu_{\mathrm{B}} = 0. \qquad 3.15.4$$

We now see that this condition can equally be expressed in terms of absolute activities in the form

$$\prod_{\mathrm{B}} (\lambda_{\mathrm{B}})^{\nu_{\mathrm{B}}} = 1. \qquad 3.15.5$$

We recall that each ν_{B} is negative for a reactant and positive for a product in the chemical equation for the process.

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* Fowler and Guggenheim, Statistical Thermodynamics, Cambridge University Press 1939 p. 66.

In particular the condition for the equilibrium distribution of a species i between the phases α and β may be written

$$\lambda_i^\alpha = \lambda_i^\beta. \qquad 3.15.6$$

We can now rewrite formulae (1.28.12), (1.28.15), and (1.28.16) as

$$R^{-1}\mathrm{d}S = (RT)^{-1}\mathrm{d}U + (P/RT)\mathrm{d}V - \sum_i \ln\lambda_i \mathrm{d}n_i \qquad 3.15.7$$

$$-R^{-1}\mathrm{d}(\text{\AE}/T) = R^{-1}\mathrm{d}J = -(U/R)\mathrm{d}(T^{-1}) + (P/RT)\mathrm{d}V - \sum_i \ln\lambda_i \mathrm{d}n_i \qquad 3.15.8$$

$$-R^{-1}\mathrm{d}(G/T) = R^{-1}\mathrm{d}Y = -(H/R)\mathrm{d}(T^{-1}) - (V/RT)\mathrm{d}P - \sum_i \ln\lambda_i \mathrm{d}n_i. \qquad 3.15.9$$

§3.16 *Thermodynamic functions of a gas*

When we set $A = RT$ in formula (3.10.5) for a gas we obtain

$$G_\mathrm{m}(T, P) - G_\mathrm{m}(T, P^\ominus) = RT\ln(P/P^\ominus) + B_2(P - P^\ominus) + \tfrac{1}{2}(RT)^{-1}(B_3 - B_2^2)(P^2 - P^{\ominus 2}). \qquad 3.16.1$$

When we set

$$\mu^\ominus(T) = G_\mathrm{m}(T, P^\ominus) - B_2 P^\ominus - \tfrac{1}{2}(RT)^{-1}(B_3 - B_2^2)P^{\ominus 2} \qquad 3.16.2$$

formula (1) simplifies to

$$\mu(T, P) = G_\mathrm{m}(T, P) = \mu^\ominus(T) + RT\ln(P/P^\ominus) + B_2 P + \tfrac{1}{2}(RT)^{-1}(B_3 - B_2^2)P^2. \qquad 3.16.3$$

Substituting (3.15.2) into (3) we obtain

$$\ln(\lambda/\lambda^\ominus) = \ln(P/P^\ominus) + B_2 P/RT + \tfrac{1}{2}(B_3 - B_2^2)(P/RT)^2 \qquad 3.16.4$$

where

$$\lambda^\ominus = \exp(\mu^\ominus/RT) \qquad 3.16.5$$

so that $\lambda^\ominus$ is a function of the temperature only.

From (3) we derive immediately

$$-S_\mathrm{m} = \mathrm{d}\mu^\ominus/\mathrm{d}T + R\ln(P/P^\ominus) + (\mathrm{d}B_2/\mathrm{d}T)P + \tfrac{1}{2}P^2\mathrm{d}(R^{-1}T^{-1}B_3 - R^{-1}T^{-1}B_2^2)/\mathrm{d}T \qquad 3.16.6$$

$$H_\mathrm{m} = \mu^\ominus - T\mathrm{d}\mu^\ominus/\mathrm{d}T + (B_2 - T\mathrm{d}B_2/\mathrm{d}T)P + \tfrac{1}{2}P^2\{R^{-1}T^{-1}B_3 - R^{-1}T^{-1}B_2^2 - T\mathrm{d}(R^{-1}T^{-1}B_3 + R^{-1}T^{-1}B_2^2)/\mathrm{d}T\}. \qquad 3.16.7$$

$\mu^\ominus$ is called the *standard chemical potential*, $-\mathrm{d}\mu^\ominus/\mathrm{d}T$ the *standard proper entropy* of gas, and $\mu^\ominus - T\mathrm{d}\mu^\ominus/\mathrm{d}T$ the *standard proper enthalpy* of gas.

In general there does not exist any state in which simultaneously $\mu = \mu^\ominus$ and $\mathrm{d}\mu/\mathrm{d}T = \mathrm{d}\mu^\ominus/\mathrm{d}T$. For this reason expressions such as ‘entropy in the standard state’ should be avoided.

§3.17 *Fugacity*

It is often convenient to use a quantity p called the *fugacity* of the gas defined* by

$$\lambda/\lambda^{\ominus} = p/P^{\ominus} \qquad 3.17.1$$

$$p/P \rightarrow 1 \quad \text{as} \quad P \rightarrow 0. \qquad 3.17.2$$

An alternative equivalent definition of p is

$$\ln p = \ln P^{\infty} + \int_{P^{\infty}}^{P} V_{\mathrm{m}} \mathrm{d}P \qquad 3.17.3$$

where P^{∞} is a pressure sufficiently small so that $p=P$. In a perfect gas the fugacity is equal to the pressure. For a real gas at moderate pressures according to (3.16.4)

$$\ln p = \ln P + B_2 P/RT + \tfrac{1}{2}(B_3 - B_2^2)(P/RT)^2. \qquad 3.17.4$$

The simplicity attained by the introduction of the fugacity is one of appearance or elegance. It leads to nothing quantitative unless we express the fugacity in terms of the pressure and then we are back where we started.

§3.18 *Gases at high temperatures*

By means of statistical mechanics the second, third, fourth, . . . virial coefficients can be expressed in terms of integrals, called 'cluster integrals', over the position coordinates of clusters of two, three, four, . . . molecules. The evaluation of these cluster integrals, except that for the second virial coefficient, is in general laborious. The effort required depends on the form of the dependence of the interaction energy w on the distance r between two molecules. The cluster integrals become much more tractable for the simplest model of non-attracting rigid spheres defined by

$$w = \infty \qquad r < \sigma \qquad 3.18.1$$

$$w = 0 \qquad r > \sigma. \qquad 3.18.2$$

For this simple model the several virial coefficients are conveniently expressed in terms of a proper volume b defined by

$$b = \tfrac{2}{3}\pi L \sigma^3 \qquad 3.18.3$$

as follows

$$B_2/b = 1 \qquad 3.18.4$$

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* Lewis, Proc. Nat. Acad. Sci. U.S. 1901 **37** 49; Z. Phys. Chem. 1901 **38** 205.

$$B_3/b^2 = 0.625 \qquad 3.18.5$$

$$B_4/b^3 = 0.287 \qquad 3.18.6$$

$$B_5/b^4 = 0.110. \qquad 3.18.7$$

This model and these virial coefficients describe the limiting behaviour of a gas at high temperatures.

A very simple formula* giving a rough approximation to the accurate virial expansion for non-attracting rigid spheres is

$$\begin{aligned} PV_\mathrm{m}/RT &= (1 - b/4V_\mathrm{m})^{-4} \\ &= 1 + 4(b/4V_\mathrm{m}) + 10(b/4V_\mathrm{m})^2 + 20(b/4V_\mathrm{m})^3 + 35(b/4V_\mathrm{m})^4 \end{aligned} \qquad 3.18.8$$

as compared with the accurate expansion†

$$PV_\mathrm{m}/RT = 1 + 4(b/4V_\mathrm{m}) + 10(b/4V_\mathrm{m})^2 + 18.36(b/4V_\mathrm{m})^3 + 28.2(b/4V_\mathrm{m})^4. \qquad 3.18.9$$

§3.19 *Slightly imperfect gases*

We shall call a gas *slightly imperfect* when the pressure or density is sufficiently low for all virial coefficients to be ignored except the second B_2. The thermodynamic properties of a slightly imperfect gas are given by the following formulae where we have dropped the subscript from B_2

$$\mu = G_\mathrm{m} = \mu^\ominus + RT\ln(P/P^\ominus) + BP \qquad 3.19.1$$

$$\ln\lambda = \ln\lambda^\ominus + \ln(P/P^\ominus) + BP/RT \qquad 3.19.2$$

$$-S_\mathrm{m} = \mathrm{d}\mu^\ominus/\mathrm{d}T + R\ln(P/P^\ominus) + (\mathrm{d}B/\mathrm{d}T)P \qquad 3.19.3$$

$$H_\mathrm{m} = \mu^\ominus - T\mathrm{d}\mu^\ominus/\mathrm{d}T + (B - T\mathrm{d}B/\mathrm{d}T)P \qquad 3.19.4$$

$$PV_\mathrm{m} = RT + PB \qquad 3.19.5$$

$$C_P = T(\partial S_\mathrm{m}/\partial T)_P = (\partial H_\mathrm{m}/\partial T) = -T\mathrm{d}^2\mu^\ominus/\mathrm{d}T^2 - TP(\mathrm{d}^2B/\mathrm{d}T^2) \qquad 3.19.6$$

$$\alpha V_\mathrm{m} = (\partial V_\mathrm{m}/\partial T)_P = R/P + \mathrm{d}B/\mathrm{d}T \qquad 3.19.7$$

$$\kappa_T V_\mathrm{m} = -(\partial V_\mathrm{m}/\partial P)_T = RT/P^2. \qquad 3.19.8$$

For the sake of brevity we shall use these formulae omitting all higher powers of P; when higher terms are required there is no difficulty in inserting them.

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* Guggenheim, Molec. Phys. 1965 **9** 199.

† Rowlinson, Rep. Prog. Phys. 1965 **28** 180.

§3.20 *Joule–Thomson coefficient*

When we discussed throttling in §3.11 we stressed the fact that at that stage we could not yet measure thermodynamic temperature. Now that we know how to do this by means of a gas thermometer, it is profitable to return to a discussion of throttling. We shall generalize this discussion by including the possibility of absorption of heat by the outflowing gas. In place of formula (3.11.3) we then have

$$H(T_2, P_2) - H(T_1, P_1) = q. \qquad 3.20.1$$

We first consider the isothermal case when q is adjusted so that $T_1 = T_2$. Formula (1) then reduces to

$$H(P_2) - H(P_1) = q \qquad (\text{const. } T) \qquad 3.20.2$$

so that measurement of q leads directly to the determination of $(\partial H/\partial P)_T$.

In the adiabatic case when $q = 0$ we have

$$H(T_2, P_2) - H(T_1, P_1) = 0. \qquad 3.20.3$$

If the pressure drop is small we may usefully replace (3) by

$$\mathrm{d}H = (\partial H/\partial T)_P \mathrm{d}T + (\partial H/\partial P)_T \mathrm{d}P = 0.$$

The ratio of the temperature fall to the pressure drop is called the *Joule–Thomson coefficient* given by

$$(\partial T/\partial P)_H = -(\partial H/\partial P)_T/(\partial H/\partial T)_P = -(\partial H_\mathrm{m}/\partial P)_T/(\partial H_\mathrm{m}/\partial T)_P$$
$$= -V_\mathrm{m}(1 - \alpha T)/C_P \qquad 3.20.4$$

by use of (1.48.4) and (3.03.2).

When we use formula (3.19.4) we obtain

$$(\partial T/\partial P)_H = (-B + T\mathrm{d}B/\mathrm{d}T)/C_P. \qquad 3.20.5$$

§3.21 *Temperature dependence of second virial coefficient*

The second virial coefficient B_2 or B is negative at low temperature, increases with temperature, and eventually becomes positive at a temperature called the *Boyle temperature* and denoted by T_B.

It is impossible to fit the quantitative dependence of B on the temperature by any two-parameter formula such as the van der Waals formula

$$B = b - aT^{-1} \qquad 3.21.1$$

or the Berthelot formula

$$B = b - cT^{-2}. \qquad 3.21.2$$

The temperature dependence of B can be fitted quantitatively by various three-parameter formulae of which the simplest is

$$B=b-aT^{-1}-cT^{-2}. \qquad 3.21.3$$

This formula is purely empirical.

To obtain a theoretical formula we have to assume a particular form for the interaction energy w between a pair of molecules as a function of their distance apart r. The simplest model, commonly called a 'square well', is described by

$$w=\infty \qquad (r<\sigma) \qquad 3.21.4$$

$$w=-\varepsilon \qquad (\sigma<r<R) \qquad 3.21.5$$

$$w=0 \qquad (r>R) \qquad 3.21.6$$

with three adjustable parameters σ, R, and ε. This model leads to the formula for the second virial coefficient

$$B=b[1-(R^3/\sigma^3-1)\{\exp(\varepsilon/kT)-1\}] \qquad 3.21.7$$

where

$$b=\tfrac{2}{3}\pi L\sigma^3. \qquad 3.21.8$$

The application to nitrogen is shown in figure 3.3 where the curve represents formula (7) with

$$b=40.3\ \mathrm{cm}^3\ \mathrm{mole}^{-1} \qquad R/\sigma=1.50 \qquad \varepsilon/k=116\ \mathrm{K}. \qquad 3.21.9$$

§3.22 *Boyle temperature and inversion temperature*

Boyle's law $PV=f(T)$ is most nearly obeyed at the temperature at which $B=0$. This temperature is accordingly called the *Boyle temperature* and it is denoted by T_B. According to formulae (3.21.7) to (3.21.9) for nitrogen $T_\mathrm{B}=330$ K. This point is shown in figure 3.3.

The Joule–Thomson coefficient for a slightly imperfect gas is positive at the lowest temperatures (cooling by throttling) but is negative at high temperatures (heating by throttling). The temperature at which the effect changes sign is called the *inversion temperature* and is denoted by T_i. According to (3.20.5) the inversion temperature is determined by

$$\mathrm{d}B/\mathrm{d}T=B/T. \qquad 3.22.1$$

When B is plotted against T the tangent through the origin touches the curve at $T=T_\mathrm{i}$. For nitrogen this is shown in figure 3.3. According to formulae (3.21.7) to (3.21.9) for nitrogen $T_\mathrm{i}=633$ K.

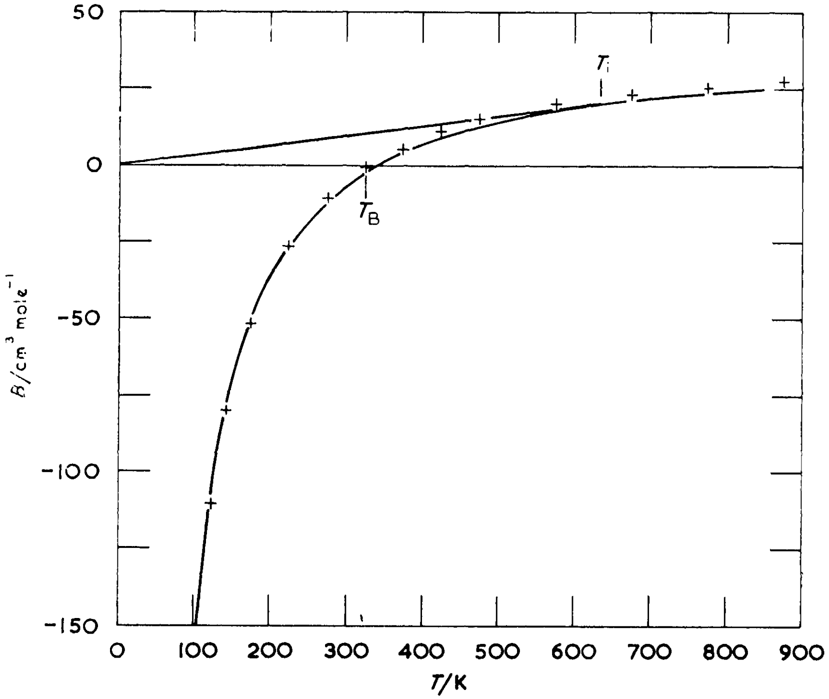

Fig. 3.3. Second virial coefficient of nitrogen, + experimental data of Holborn and Otto*, — formulae (3.21.7) to (3.21.9)

§3.23 *Relation between heat capacities of slightly imperfect gas*

We have the general relation (3.07.3)

$$C_P - C_V = \alpha^2 T V_{\text{m}} / \kappa_T. \qquad 3.23.1$$

Using formulae (3.19.5), (3.19.7), and (3.19.8) we deduce

$$C_P - C_V = R(1 + R^{-1} P \mathrm{d}B/\mathrm{d}T)^2. \qquad 3.23.2$$

§3.24 *Adiabatic change of a gas*

For an adiabatic change we have from (3.08.2) and (3.08.3)

$$-\mathrm{d}\ln V/\mathrm{d}P = \kappa_S = \kappa_T C_V/C_P \qquad (S \text{ constant}). \qquad 3.24.1$$

This differential equation for an adiabatic change cannot be integrated unless the right hand side can be expressed as an explicit function of P, V

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* Holborn and Otto, Z. Phys. 1925 **33** 5.

and not necessarily even then. In the approximation of a perfect gas (1) becomes

$$-\mathrm{d}\ln V/\mathrm{d}\ln P = C_V/C_P \qquad (S \text{ constant}). \qquad 3.24.2$$

In the special case of a gas with monatomic molecules

$$C_V/R = \tfrac{3}{2} \qquad C_P/R = \tfrac{5}{2} \qquad \text{(monatomic molecules)} \qquad 3.24.3$$

so that (2) becomes

$$\mathrm{d}\ln V/\mathrm{d}\ln P = -\tfrac{3}{5} \qquad \text{(monatomic molecules)} \qquad 3.24.4$$

which can be integrated to

$$PV^{\frac{5}{3}} = \text{constant}. \qquad 3.24.5$$

In other cases (2) cannot be integrated explicitly.

§3.25 *Temperature dependence of $\mu^{\ominus}$ and $\lambda^{\ominus}$*

In §3.16 we have expressed all the most important thermodynamic functions of a gas in terms of $\mu^{\ominus}$ or $\lambda^{\ominus}$ each of these being a function of temperature only. We shall now consider this temperature dependence.

In the first place $\mu^{\ominus}$ contains an arbitrary constant term which we denote by H^0. There is a corresponding term H^0 in H_m and a corresponding factor $\exp(H^0/RT)$ in $\lambda^{\ominus}$. As long as chemical reactions are excluded we may fix H^0 arbitrarily for each substance, for example by setting $H^0 = 0$ at 25 °C. If on the contrary chemical processes are admissible then the values of H^0 for all substances are not independent. We may however fix H^0 arbitrarily for each element. The commonly accepted convention is $H^0 = 0$ for every element in its stable form at 25 °C.

There is also an arbitrary constant term in $-\mathrm{d}\mu^{\ominus}/\mathrm{d}T$ which we denote by S^0. As long as chemical reactions are excluded we may fix S^0 arbitrarily for each substance, for example by setting $S \to 0$ as $T \to 0$. If on the contrary chemical reactions are admissible then the values of S^0 for all substances are not independent. We may however fix S^0 arbitrarily for each element. The accepted convention is $S \to 0$ as $T \to 0$ for every element in its stable form. There are complications in the case of hydrogen which will be discussed in §3.56. When these conventions for H^0 and S^0 are used the chemical potential is called the *conventional chemical potential* and the entropy is called the *conventional entropy*.

In classical thermodynamics the accepted convention for S^0 is on a par with that for H^0, but statistical thermodynamics supplements the former convention in two ways. Firstly it provides a simple physical interpretation of the convention for S^0 which will be given in §3.53. Secondly by use of this interpretation of the convention it provides explicit formulae for the conventional entropy of gases. These formulae will be quoted without derivation in §§3.26–3.29 and interpreted later.

§3.26 *Monatomic molecules*

For gases having monatomic molecules, when we use the conventions specified in §3.25, it can be shown by statistical thermodynamics that

$$\lambda^{\ominus}=\exp(\mu^{\ominus}/RT)=\exp(H^0/RT)\,L^4h^3P^{\ominus}/g_0(2\pi M)^{\frac{3}{2}}(RT)^{\frac{5}{2}} \qquad 3.26.1$$

where g_0 denotes the degree of degeneracy of the ground electronic level of the free atom. The value of g_0 is 1 for the noble gases He, Ne, Ar, Kr, Xe, Rn, and for Zn, Cd, Hg; its value is 2 for the alkali metals Li, Na, K, Rb, Cs.

When we use (1) in the formulae of §3.19 the conventional values of μ, λ, and S_{m} for a slightly imperfect gas are given by

$$\mu=G_{\mathrm{m}}=H^0-RT\ln g_0+RT\ln\{L^4h^3P^{\ominus}/(2\pi M)^{\frac{3}{2}}(RT)^{\frac{5}{2}}\}+RT\ln(P/P^{\ominus})+BP \qquad 3.26.2$$

$$\ln\lambda=H^0/RT-\ln g_0+\ln\{L^4h^3P^{\ominus}/(2\pi M)^{\frac{3}{2}}(RT)^{\frac{5}{2}}\}+\ln(P/P^{\ominus})+BP/RT \qquad 3.26.3$$

$$S_{\mathrm{m}}=R\ln g_0-R\ln\{L^4h^3P^{\ominus}/(2\pi M)^{\frac{3}{2}}(RT)^{\frac{5}{2}}\}+\tfrac{5}{2}R-R\ln(P/P^{\ominus})-P(\mathrm{d}B/\mathrm{d}T). \qquad 3.26.4$$

If the gas is more than slightly imperfect it is a straightforward matter to include terms in the higher virial coefficients $B_3, B_4, \ldots$.

§3.27 *Numerical values in entropy constant*

We shall now insert numerical values for the constants in the formulae of §3.26 taking as our standard pressure $P^{\ominus}=1$ atm. We have

$$h=6.6256\times10^{-34}\ \mathrm{J\ s}$$
$$R=8.3143\ \mathrm{J\ K^{-1}\ mole^{-1}}$$
$$L=0.60225\times10^{24}\ \mathrm{mole^{-1}}$$
$$P^{\ominus}=1\ \mathrm{atm}=1.01325\times10^{5}\ \mathrm{J\ m^{-3}}.$$

With these values we obtain

$$L^4h^3P^{\ominus}/(2\pi M)^{\frac{3}{2}}(RT)^{\frac{5}{2}}=1.236(\mathrm{kg/mole})^{\frac{3}{2}}(T/\mathrm{K})^{-\frac{5}{2}}$$
$$=39.03(\mathrm{g/mole})^{\frac{3}{2}}(T/\mathrm{K})^{-\frac{5}{2}}=(\mathrm{g/mole})^{\frac{3}{2}}(T/4.333\ \mathrm{K})^{-\frac{5}{2}}. \qquad 3.27.1$$

Using (1) in the formulae of §3.26 we obtain

$$\ln \lambda^\ominus = \mu^\ominus/RT = H^0/RT - \ln g_0 - \tfrac{3}{2}\ln(M/\text{g mole}^{-1}) - \tfrac{5}{2}\ln(T/4.333\,\text{K}) \qquad 3.27.2$$

$$\ln \lambda = \mu/RT = H^0/RT - \ln g_0 - \tfrac{3}{2}\ln(M/\text{g mole}^{-1}) \\ - \tfrac{5}{2}\ln(T/4.333\ \text{K}) + \ln(P/\text{atm}) + BP/RT \qquad 3.27.3$$

$$S_\text{m}/R = \ln g_0 + \tfrac{5}{2} + \tfrac{3}{2}\ln(M/\text{g mole}^{-1}) + \tfrac{5}{2}\ln(T/4.333\ \text{K}) \\ - \ln(P/\text{atm}) - (P/R)\text{d}B/\text{d}T \\ = \ln g_0 + \tfrac{3}{2}\ln(M/\text{g mole}^{-1}) + \tfrac{5}{2}\ln(T/1.594\ \text{K}) \\ - \ln(P/\text{atm}) - (P/R)\text{d}B/\text{d}T \\ = 10.35 + \ln g_0 + \tfrac{3}{2}\ln(M/\text{g mole}^{-1}) + \tfrac{5}{2}\ln(T/100\ \text{K}) \\ - \ln(P/\text{atm}) - (P/R)\text{d}B/\text{d}T \qquad 3.27.4$$

$$H_\text{m} = H^0 + \tfrac{5}{2}RT + (B - T\text{d}B/\text{d}T)P \qquad 3.27.5$$

$$C_P/R = \tfrac{5}{2} - T(\text{d}^2B/\text{d}T^2)P/R. \qquad 3.27.6$$

§3.28 *Linear molecules*

In the formulae for monatomic molecules the electronic degrees of freedom were taken care of by g_0 while the remaining factor in $\lambda^\ominus$ or term in $\mu^\ominus$ relates to the translational degrees of freedom. In polyatomic molecules there are the same factors in $\lambda^\ominus$ and further factors to take care of the rotational and vibrational degrees of freedom. We shall describe these factors first for linear molecules and then for non-linear molecules.

For linear molecules the extra factor in $\lambda^\ominus$ due to the rotational degrees of freedom is at ordinary temperatures

$$\lambda_\text{rot} = (s\Theta_\text{r}/T)\{1 + \Theta_\text{r}/3T + \Theta_\text{r}^2/15T^2\}^{-1} \qquad (T \gg \Theta_\text{r}) \qquad 3.28.1$$

where Θ_r is a rotational characteristic temperature inversely proportional to the moment of inertia I of the molecule and defined by

$$\Theta_\text{r} = h^2/8\pi^2 Ik. \qquad 3.28.2$$

The factor s called *symmetry number* is 2 for a symmetrical linear molecule and 1 for an unsymmetrical molecule.

The rotational term in $\mu^\ominus$ is

$$\mu_\text{rot} = RT\ln\lambda_\text{rot} = RT\ln(s\Theta_\text{r}/T) - RT\ln\{1 + \Theta_\text{r}/3T + \Theta_\text{r}^2/15T^2\} \\ = RT\ln(s\Theta_\text{r}/T) - \tfrac{1}{3}R\Theta_\text{r} - R\Theta_\text{r}^2/90T. \qquad 3.28.3$$

The constant term $-\tfrac{1}{3}R\Theta_\text{r}$ may be absorbed into H^0 and (3) then becomes

$$\mu_\text{rot} = RT\ln(s\Theta_\text{r}/T) - R\Theta_\text{r}^2/90T. \qquad 3.28.4$$

The corresponding rotational contributions to S_m, H_m, and C are

$$S_\mathrm{rot}=R-R\ln(s\Theta_\mathrm{r}/T)+R\Theta_\mathrm{r}^2/90T^2 \tag{3.28.5}$$

$$H_\mathrm{rot}=RT-R\Theta_\mathrm{r}^2/45T \tag{3.28.6}$$

$$C_\mathrm{rot}=R+R\Theta_\mathrm{r}^2/45T^2. \tag{3.28.7}$$

We now turn to the vibrational contributions. A linear molecule composed of a atoms has $3a-5$ normal vibrational modes each having a characteristic frequency ν_i. Associated with the frequency ν_i is a vibrational characteristic temperature $\Theta_{\mathrm{v}i}$ defined by

$$k\Theta_{\mathrm{v}i}=h\nu_i. \tag{3.28.8}$$

The vibrational contributions to the several thermodynamic functions are

$$\mu_\mathrm{vib}=RT\ln\lambda_\mathrm{vib}=RT\sum_i\ln\{1-\exp(-\Theta_{\mathrm{v}i}/T)\} \tag{3.28.9}$$

$$S_\mathrm{vib}=R\sum_i\Theta_{\mathrm{v}i}/T\{\exp(\Theta_{\mathrm{v}i}/T)-1\}-R\sum_i\ln\{1-\exp(-\Theta_{\mathrm{v}i}/T)\} \tag{3.28.10}$$

$$H_\mathrm{vib}=R\sum_i\Theta_{\mathrm{v}i}/\{\exp(\Theta_{\mathrm{v}i}/T)-1\} \tag{3.28.11}$$

$$C_\mathrm{vib}=R\sum_i\{(\Theta_{\mathrm{v}i}/2T)/\sinh(\Theta_{\mathrm{v}i}/2T)\}^2. \tag{3.28.12}$$

We have still to discuss the electronic factor g_0. For the vast majority of linear molecules regarded as saturated g_0 is unity. The outstanding exceptions are O_2 and NO. The ground state of O_2 is $^3\Sigma$ and $g_0=3$. The odd molecule NO has a ground state $^2\Pi_{\frac{1}{2}}$ and an excited state $^2\Pi_{\frac{3}{2}}$ having an excitation energy ε such that ε/k is only 178 K. As a result of this the constant g_0 has to be replaced by the temperature dependent factor

$$2+2\exp(-178\ \mathrm{K}/T) \tag{3.28.13}$$

having an effective value 2 when $T \ll 178$ K and 4 when $T \gg 178$ K.

Values of Θ_r, Θ_v, s, and g_0 are given* in table 3.1 for the commonest diatomic molecules and in table 3.2 for a few other typical linear molecules.

§3.29 *Non-linear molecules*

Whereas a linear molecule has 2 rotational degrees of freedom, a non-linear molecule has 3. For a non-linear molecule the rotational characteristic

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* Values taken from Herzberg, Spectra of Diatomic Molecules, Van Nostrand 1950. Cf. Fowler and Guggenheim, Statistical Thermodynamics, Cambridge University Press 1939 p. 90. Cf. Slater, Introduction to Chemical Physics, McGraw-Hill 1939 p. 136, observing that their Θ_rot is equal to twice our Θ_r.

TABLE 3.1

Characteristic temperatures Θ_r and Θ_v, symmetry numbers s, and electronic weights g_0 for typical diatomic molecules

Formula	Θ_r/K	$10^{-2}\Theta_v$/K	s	g_0
H_2	85.3	59.8	2	1
D_2	42.7	43.0	2	1
N_2	2.88	33.5	2	1
O_2	2.07	22.4	2	3
CO	2.77	30.8	1	1
NO	2.44	27.0	1	–
HCl	15.0	41.5	1	1
HBr	12.0	36.8	1	1
HI	9.29	32.1	1	1
Cl_2	0.344	7.96	2	1
Br_2	0.116	4.62	2	1
I_2	0.0537	3.07	2	1

TABLE 3.2

Characteristic temperatures Θ_r and Θ_{vi}, symmetry numbers s, and electronic weights g_0 for typical polyatomic linear molecules

Formula	Θ_r/K	$10^{-2}\Theta_{vi}$/K	s	g_0
OCO	0.560	9.60 9.60 20.0 33.8	2	1
NNO	0.602	8.47 8.47 18.5 32.0	1	1
HCCH	1.69	8.80 8.80 10.5 10.5 28.4 47.3 48.5	2	1
HCN	2.13	10.5 10.5 28.7 49.5	1	1

temperature Θ_r is related to the 3 principal moments of inertia I_1, I_2, I_3 by

$$\Theta_r = h^2/8\pi^2(I_1 I_2 I_3)^{\frac{1}{3}}k. \qquad 3.29.1$$

The rotational factor in $\lambda^\ominus$ at ordinary temperatures is given by

$$\lambda_{rot} = s\Theta_r^{\frac{3}{2}}/\pi^{\frac{1}{2}}T^{\frac{3}{2}}. \qquad 3.29.2$$

The symmetry number s is defined as the number of indistinguishable orientations of the molecule. For example s is 1 for NOCl, 2 for OH_2, 3 for NH_3, 4 for C_2H_4, 6 for BF_3, and 12 for C_6H_6. The rotational contributions to the several thermodynamic functions are

$$\mu_{rot} = RT \ln \lambda_{rot} = RT \ln(s\Theta_r^{\frac{3}{2}}/\pi^{\frac{1}{2}}T^{\frac{3}{2}}) \qquad 3.29.3$$

$$S_{rot} = \tfrac{3}{2}R - R \ln(s\Theta_r^{\frac{3}{2}}/\pi^{\frac{1}{2}}T^{\frac{3}{2}}) \qquad 3.29.4$$

$$U_{rot} = \tfrac{3}{2}RT \qquad 3.29.5$$

$$C_{rot} = \tfrac{3}{2}R. \qquad 3.29.6$$

The vibrational contributions are exactly as for linear molecules except that there are $3a$–6 normal vibrational modes instead of $3a$–5. Thus we have

$$S_{vib} = R\sum_i \Theta_{vi}/T\{\exp(\Theta_{vi}/T)-1\} - R\sum_i \ln\{1-\exp(-\Theta_{vi}/T)\}. \qquad 3.29.7$$

The value of g_0 is unity for almost all non-linear molecules including OH_2, SH_2, NH_3, PH_3, CH_4, SO_2, and all organic molecules. Its value for free radicals such as CH_3, C_6H_5, is 2.

TABLE 3.3

Characteristic temperatures Θ_r and Θ_{vi}, symmetry numbers s, and electronic weights g_0 for typical non-linear molecules

	Formula	Θ_r/K	$10^{-2}\Theta_{vi}$/K	s	g_0
*	NOCl		4.8 8.6 25.9	1	1
	OH_2	22.3	22.9 52.5 54.0	2	1
	NH_3	12.3	13.7 23.4 23.4 48.0 49.1 49.1	3	1

* Landau and Fletcher, J. Molec. Spect. 1960 **4** 280.

Values of Θ_r, Θ_{vi}, s, and g_0 for a few non-linear molecules are given* in table 3.3.

Table 3.4 gives the vibrational contributions of a single normal mode to the several thermodynamic functions in terms of $x=\Theta_v/T$.

§3.30 *Pressure dependence for condensed phases*

We turn now from gases to condensed phases. Later we shall consider equilibrium between a condensed phase and a gas. As we shall see in §3.44 there are conditions of temperature and pressure called critical at which the distinction between gas and liquid disappears, but except at conditions close to the critical there is a rather sharp contrast between the properties of a gas and a liquid. The contrast between a crystal and a fluid, either gas or liquid, is always a sharp one.

Whereas the isothermal compressibility of a gas is roughly equal to the reciprocal of the pressure, the isothermal compressibility of a solid and that of a liquid, except near the critical temperature, is much smaller than that of a gas and is less dependent on the pressure. We accordingly use the approximation

$$-V^{-1}(\partial V/\partial P)_T=\kappa_T=\text{const.} \qquad 3.30.1$$

We can integrate (1) at constant temperature, obtaining

$$V_m=V^{\ominus}\exp\{-\kappa_T(P-P^{\ominus})\} \qquad 3.30.2$$

where $V^{\ominus}$ is the value of V_m at the standard pressure $P^{\ominus}$, usually one atmosphere.

For typical liquids κ_T is about 10^{-4} atm^{-1} and for many solids is even smaller. We may therefore, without appreciable loss of accuracy replace (2) by the more convenient relation

$$V_m=V^{\ominus}\{1-\kappa_T(P-P^{\ominus})\}. \qquad 3.30.3$$

We can integrate again with respect to P at constant T obtaining

$$\mu=\mu^{\ominus}+V^{\ominus}\{(P-P^{\ominus})-\tfrac{1}{2}\kappa_T(P-P^{\ominus})^2\}. \qquad 3.30.4$$

It is sometimes convenient to rewrite (4) as

$$\mu=\mu^{\ominus}+(P-P^{\ominus})\,\tfrac{1}{2}(V_m+V^{\ominus}). \qquad 3.30.5$$

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* Values taken from Herzberg, Infra-red and Raman Spectra, Van Nostrand 1945. Cf. Fowler and Guggenheim, Statistical Thermodynamics, Cambridge University Press 1939 pp. 113–114.

TABLE 3.4

Contributions of a single harmonic oscillator to the several thermodynamic quantities expressed as functions of $x = h\nu/kT = \Theta_v/T$

x	$-\mu/RT$ $= -\ln\{1-\exp(-x)\}$	H_m/RT $= x/(\exp x-1)$	S_m/R $= (H_m-\mu)/RT$	C/R $= \{\frac{1}{2}x/\sinh \frac{1}{2}x\}^2$
0.01	4.610	0.995	5.605	1.000
0.05	3.021	0.975	3.996	1.000
0.1	2.352	0.951	3.303	0.999
0.2	1.708	0.903	2.611	0.997
0.3	1.350	0.857	2.208	0.993
0.4	1.110	0.813	1.923	0.987
0.5	0.933	0.771	1.704	0.979
0.6	0.796	0.730	1.526	0.971
0.7	0.686	0.691	1.377	0.960
0.8	0.597	0.653	1.249	0.948
0.9	0.522	0.617	1.138	0.935
1.0	0.459	0.582	1.041	0.921
1.1	0.405	0.549	0.954	0.905
1.2	0.358	0.517	0.876	0.888
1.3	0.318	0.487	0.805	0.870
1.4	0.283	0.458	0.741	0.852
1.5	0.252	0.431	0.683	0.832
1.6	0.226	0.405	0.630	0.811
1.7	0.202	0.380	0.582	0.790
1.8	0.181	0.356	0.537	0.769
1.9	0.162	0.334	0.496	0.747
2.0	0.145	0.313	0.458	0.724
2.1	0.131	0.293	0.424	0.701
2.2	0.117	0.274	0.392	0.678
2.3	0.106	0.256	0.362	0.655
2.4	0.095	0.239	0.335	0.632
2.5	0.086	0.224	0.309	0.609
2.6	0.077	0.209	0.286	0.586
2.7	0.070	0.195	0.264	0.563
2.8	0.063	0.181	0.244	0.540
2.9	0.057	0.169	0.225	0.518
3.0	0.051	0.157	0.208	0.496
3.2	0.042	0.136	0.178	0.454
3.4	0.034	0.117	0.151	0.413
3.6	0.028	0.101	0.129	0.374
3.8	0.023	0.087	0.110	0.338
4.0	0.018	0.075	0.093	0.304
4.5	0.011	0.051	0.062	0.230
5.0	0.007	0.034	0.041	0.171
5.5	0.004	0.023	0.027	0.125
6.0	0.002	0.015	0.017	0.090
6.5	0.002	0.010	0.013	0.064
7.0	0.001	0.006	0.007	0.045

Differentiating (5) with respect to T at constant pressure we obtain

$$\begin{aligned} S_m &= -d\mu^\ominus/dT-(P-P^\ominus)\,\tfrac{1}{2}(\partial V_m/\partial T+\partial V^\ominus/\partial T) \\ &= -d\mu^\ominus/dT-(P-P^\ominus)\,\tfrac{1}{2}(\alpha V_m+\alpha^\ominus V^\ominus) \end{aligned} \qquad 3.30.6$$

where α and $\alpha^\ominus$ are the coefficients of thermal expansion at pressures P and $P^\ominus$ respectively.

From (5) and (6) we derive

$$H_m=\mu+TS_m=\mu^\ominus-T\,d\mu^\ominus/dT+(P-P^\ominus)\,\tfrac{1}{2}\{V_m(1-\alpha T)+V^\ominus(1-\alpha^\ominus T)\} \qquad 3.30.7$$

and

$$C=T\,d^2\mu^\ominus/dT^2-(P-P^\ominus)\,\tfrac{1}{2}T\{V_m d\alpha/dT+V^\ominus d\alpha^\ominus/dT\}. \qquad 3.30.8$$

§3.31 *Temperature dependence for liquids*

We have seen that the dependence of the thermodynamic properties of condensed phases on the pressure is simple and usually small. We have now to consider how these properties depend on the temperature.

As regards liquids there is nothing fundamental or general that can be said except that $\mu^\ominus$ can often be represented over quite a wide range of temperature by an empirical relation of the form

$$\mu^\ominus=A-(B-C)T-CT\ln T \qquad (A, B, C \text{ const.}). \qquad 3.31.1$$

From (1) we deduce

$$S^\ominus=-d\mu^\ominus/dT=B+C\ln T \qquad 3.31.2$$

$$H^\ominus=A+CT. \qquad 3.31.3$$

According to this empirical approximation the proper heat capacity C at the standard pressure $P^\ominus$ is independent of the temperature. We have already mentioned in §3.03 that for many liquids, in particular water, C is nearly independent of the temperature.

The approximate constancy of C and the consequent validity of relations of the form (1), (2), (3) also hold for many solids at ordinary and higher temperatures, but not at low temperatures. This accident has in the past caused undue importance to be attached to the heat capacity, in contrast to the enthalpy H and the entropy S. The only real importance of C is that it is the connecting link between H and S, as explained in §3.02. This link is especially simple when C is independent of T, but this occurrence, however frequent, is of no fundamental importance.

§3.32 *Crystals at very low temperatures*

It is predicted by statistical theory and borne out by experiment that at very low temperatures the enthalpy of a crystalline solid varies linearly with the fourth power of the thermodynamic temperature. That is to say, neglecting the small dependence on pressure,

$$H_{\mathrm{m}}=H_{\mathrm{m}}^{0}+\tfrac{1}{4}aT^{4} \qquad \text{(small } T\text{)} \qquad 3.32.1$$

where a is a constant and H_{m}^{0} is the limiting value of H_{m} as $T \to 0$. Correspondingly we have for the entropy

$$S_{\mathrm{m}}=S_{\mathrm{m}}^{0}+\tfrac{1}{3}aT^{3} \qquad \text{(small } T\text{)} \qquad 3.32.2$$

where S_{m}^{0} is the limiting value of S_{m} as $T \to 0$. The formulae (1) and (2) are not independent, but are related through the thermodynamic formula (3.02.3)

$$T\mathrm{d}S=\mathrm{d}H \qquad \text{(const. } P\text{).} \qquad 3.32.3$$

From (1) and (2) it immediately follows that

$$\mu=H_{\mathrm{m}}^{0}-TS_{\mathrm{m}}^{0}-\tfrac{1}{12}aT^{4} \qquad \text{(small } T\text{).} \qquad 3.32.4$$

We have not stated how small T must be for these formulae to hold, nor is it possible to make any precise statement since the requirement is different for different substances. For most substances investigated these formulae appear to be at least approximately valid at temperatures below 15 K.

We shall see later that a comparison between the constant S_{m}^{0} in (2) and the constant $-\mathrm{d}\mu^{\ominus}/\mathrm{d}T$ occurring in the formula for the proper entropy of a gas is of considerable interest. For this reason it is important to be able to extrapolate experimental data on the entropy from the lowest experimental temperature down to 0 K. For this purpose one determines a suitable value of the constant a from the relation (1) by plotting H against T^4 in the lowest temperature range in which experimental measurements have been made. This value of a is then used in (2) to give experimental values of $S(T)-S(0)$. Provided the experimental data extend below 15 K, the contribution to S from this extrapolation is usually so small that an accurate estimate of a is not required.

Actually the most important feature of the formulae of this section is not their precise form, still less the value of a, but the fact that S tends rapidly towards a constant value as T decreases. This behaviour is in striking contrast with the formulae for the entropy of gases at ordinary temperatures which contain terms in $\ln T$.

§3.33 *Crystals at intermediate temperatures. Debye's approximation*

In the previous section we have described the thermodynamic behaviour of crystals at very low temperatures. In §3.31 we mentioned briefly that at ordinary and higher temperatures the behaviour of many solids, as well as liquids, is represented at least approximately by the formulae of that section corresponding to a temperature-independent heat capacity. In the intermediate range the heat capacity increases with temperature, but its rate of increase falls rather rapidly. There is no precise quantitative theory except for the simplest crystals consisting of monatomic molecules. Even for these the accurate theory is so complicated as to be of little practical use and it is in fact usually replaced by a much simpler approximation due to Debye.

We shall not here describe Debye's model, still less discuss* its limitations, but shall give the formulae which follow from it. The formulae contain apart from the temperature T, two parameters namely the energy U_m^0 of the crystal at $T=0$ and a characteristic temperature Θ_D. Both these parameters U_m^0 and Θ_D are functions of the proper volume V_m, but are independent of the temperature. In considering Debye's model it is therefore expedient to regard as independent variables T, V instead of the usually more practically convenient T, P. We accordingly begin by writing down Debye's formula for the proper Helmholtz function of a crystal

$$Æ_\mathrm{m} = U_\mathrm{m} - TS_\mathrm{m} = U_\mathrm{m}^0 - TS_\mathrm{m}^0 + 3RT\int_0^{\Theta_\mathrm{D}} \ln\{1-\exp(-\theta/T)\}(3\theta^2/\Theta_\mathrm{D}^3)\mathrm{d}\theta \qquad 3.33.1$$

wherein we repeat that U_m^0 and Θ_D are functions of V_m whereas S_m^0 on the other hand is a constant independent of V_m, as well as of T, and depends only on the arbitrary zero of entropy.

From (1) we could derive the pressure by the relation

$$P = -\partial Æ/\partial V. \qquad 3.33.2$$

We have however seen in §3.30 that the thermodynamic properties of a condensed phase, in particular a crystal, are nearly independent of the pressure; more precisely $PV_\mathrm{m} \ll RT$. We may consequently regard the pressure as negligible and replace (2) by the condition

$$\partial Æ/\partial V = 0 \qquad 3.33.3$$

which gives an equilibrium relation between U^0 and Θ_D. From (1) and (3) we find that this relation is

$$\frac{\partial U_\mathrm{m}^0}{\partial V_\mathrm{m}} = 3R\frac{\partial \Theta_\mathrm{D}}{\partial V_\mathrm{m}}\int_0^{\Theta_\mathrm{D}} \frac{1}{\exp(\theta/T)-1}\,\frac{3\theta^3}{\Theta_\mathrm{D}^4}\,\mathrm{d}\theta. \qquad 3.33.4$$

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* Blackman, Rep. Progr. Phys. 1942 **8** 11.

From (1) we can derive formulae for the other thermodynamic functions, in particular

$$S_m - S_m^0 = -3R\int_0^{\Theta_D}\left[\ln\{1-\exp(-\theta/T)\} - \frac{\theta/T}{\exp(\theta/T)-1}\right]\frac{3\theta^2}{\Theta_D^3}\,d\theta \qquad 3.33.5$$

$$U_m - U_m^0 = 3R\int_0^{\Theta_D}\frac{1}{\exp(\theta/T)-1}\,\frac{3\theta^3}{\Theta_D^3}\,d\theta \qquad 3.33.6$$

$$C_V = 3R\int_0^{\Theta_D}\left\{\frac{\theta/2T}{\sinh(\theta/2T)}\right\}^2\frac{3\theta^2}{\Theta_D^3}\,d\theta. \qquad 3.33.7$$

We may note that at very low temperatures, $T \ll \Theta_D$ and we may without sensible error replace the upper limits of integration in the above formulae by ∞. We thus obtain

$$U_m - U_m^0 = 3R\frac{T^4}{\Theta_D^3}\int_0^{\infty}\frac{3\xi^3\,d\xi}{\exp\xi-1} = \frac{3\pi^4RT^4}{5\Theta_D^3} \qquad 3.33.8$$

which, in view of the negligible difference between U_m and H_m is in agreement with (3.32.1) with a given by

$$\tfrac{1}{4}a = \frac{3\pi^4R}{5\Theta_D^3}. \qquad 3.33.9$$

While we shall not here discuss the extent of agreement or disagreement to be expected between these formulae and the behaviour of real crystals, we shall however devote some space to the consideration of how the comparison can most directly be made. Let us therefore consider which quantities are most directly measurable, bearing in mind that with all condensed phases it is convenient to make measurements at constant pressure but extremely difficult to make measurements at constant volume.

The usual calorimetric measurements determine directly how H depends on T. Provided these measurements have been carried to a low enough temperature, the extrapolation to $T=0$ can be performed as described in §3.32 so that we know $H_m(T)-H_m^0$ as a function of T. Then by using the relation (3.32.3) we can without any further experimental data compute $S_m(T)-S_m^0$. We can now compare this experimental quantity with the right side of (5), which is tabulated as a function of Θ_D/T. We thus obtain for each temperature T a value of Θ_D fitting the experimental value of $S_m - S_m^0$. These values of Θ_D will be constant neither in practice, nor according to Debye's model. For we are considering data at constant pressure, consequently at varying volume, and, as the volume varies, so Θ_D varies. In fact

TABLE 3.5

Comparison of proper entropy of gold with Debye's formula

T/K	$(S_\mathrm{m}—S_\mathrm{m}^0)/R$ expt.	Θ_D/T	$\Theta_\mathrm{D}/\mathrm{K}$
15	0.06	10.90	163
20	0.14	8.25	165
30	0.385	5.57	167
40	0.705	4.225	167
50	1.05	3.39	170
60	1.40	2.87	172
70	1.73	2.45	171
80	2.03	2.15	172
90	2.32	1.91	172
100	2.58	1.72	172
120	3.07	1.44	173
140	3.49	1.23	172
160	3.87	1.075	172
180	4.22	0.95	171
200	4.53	0.855	171
300	5.77	0.555	167

TABLE 3.6

Comparison of proper entropy of magnesium with Debye's formula

T/K	$(S_\mathrm{m}—S_\mathrm{m}^0)/R$ expt.	Θ_D/T	$\Theta_\mathrm{D}/\mathrm{K}$
20	0.01	18.0	360
30	0.05	11.5	345
40	0.13	8.38	335
50	0.26	6.53	326
60	0.41	5.41	324
80	0.77	4.03	322
100	1.15	3.22	322
120	1.52	2.68	322
140	1.87	2.30	322
160	2.20	2.00	320
180	2.50	1.78	320
200	2.76	1.61	322
300	7.77	1.06	318

as the volume increases, theory predicts that Θ_D should steadily decrease. If then it is found that as T increases, the value of Θ_D, determined as described above, slowly but steadily decreases then we may say that at least there is no contradiction between the experimental data and the model. If on the other hand as T increases, the value of Θ_D thus determined increases or fluctuates, then we may say with certainty that the experimental data are in disagreement with the model.

We give typical illustrations of this method of comparison in tables 3.5 and 3.6 for gold* and magnesium† respectively. We observe that for gold Θ_D rises from 163 K to 173 K and then falls again to 167 K. For magnesium Θ_D decreases steadily from 360 K to 318 K. In a few cases, such as copper and lead, Θ_D varies even less than in the case of gold. In other cases, notably lithium, Θ_D varies by nearly 20 %.

We must emphasize that the entropy is the only simple thermodynamic function for which we have both a closed formula and an experimental value obtainable from a single set of calorimetric measurements performed at constant pressure. In spite of the directness and simplicity of the above method of comparison, it is not generally used. The usual procedure is, from the experimental measurements of H_m as a function of T, first to compute $\mathrm{d}H/\mathrm{d}T = C_P$; then by measured, or estimated values of α and κ_T to use formula (3.07.3) or (3.08.5) to compute C_V from C_P; lastly to compare the C_V so calculated with formula (7). There are two objections to this procedure as compared with that recommended here. In the first place the computation of C_P from H involves a differentiation and so increases any experimental errors whereas in the computation of S from H the integration helps to smooth out the errors introduced by the differentiation. In the second place the computation of C_V from C_P by (3.07.3) or (3.08.5) requires either several other pieces of difficult experimental measurement or else some guess work, neither of which is required if one makes comparisons of entropy. When the value of C_V, thus computed or estimated, is compared with formula (7) we can calculate at each temperature a value of Θ_D which fits. Just as in the comparison of entropies, these values of Θ_D should, if the model is good, decrease slowly and steadily as the temperature, and so the volume, increases. There appears to be a widespread, but mistaken, belief that Θ_D should be independent of temperature in spite of the thermal expansion.

Quite apart from the change in Θ_D due to thermal expansion, variations of Θ_D with temperature are to be expected owing to the limitations of Debye's model. In view of all the complications in the lattice theory, Debye's theory is remarkable not in the extent of its failure, but rather in the extent of its success‡.

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* Clusius and Harteck, Z. Phys. Chem. 1928 **134** 243.

† Clusius and Vaughen, J. Amer. Chem. Soc. 1930 **52** 4686.

‡ Blackman, Rep. Progr. Phys. 1942 **8** 11.

§3.34 *Corresponding temperatures of crystals*

We have seen that Debye's model is only an approximate representation of a simple crystal of monatomic molecules and further that even if it were an accurate representation, the characteristic temperature Θ_D should still vary with temperature owing to thermal expansion. Nevertheless it is an experimental fact that Debye's formulae with constant Θ_D do give a remarkably good approximate representation over a wide temperature range of the actual behaviour of many simple crystals, especially metals crystallizing in the cubic system. For such substances the values of $S_m - S_m^0$, of $(H_m - H_m^0)/T$, and consequently of $G_m - G_m^0$ are universal functions of T/Θ_D. Thus several important thermodynamic properties of different crystals have the same value when T/Θ_D has the same value. Temperatures of different substances such that T/Θ_D has the same value are called *corresponding temperatures.* The principle that certain thermodynamic properties have equal values for different substances at corresponding temperatures is called a *principle of corresponding temperatures.* It is to be observed that this principle for simple crystals makes no reference to the pressure, which is tacitly assumed to be low and to have no appreciable effect on the values of the properties under discussion. In §3.48 we shall discuss a more interesting principle of corresponding temperatures and corresponding pressures for liquids and gases.

§3.35 *Comparison of Debye's functions with Einstein's functions*

Debye's model was preceded by a simpler model due to Einstein leading to the simpler formulae

$$U_m - TS_m = U_m^0 - TS_m^0 + 3RT \ln\{1 - \exp(-\Theta_E/T)\} \qquad 3.35.1$$

$$U_m = U_m^0 + 3R\Theta_E/\{\exp(\Theta_E/T) - 1\} \qquad 3.35.2$$

$$S_m = S_m^0 - 3R[\ln\{1 - \exp(\Theta_E/T)\} - \Theta_E/T\{\exp(\Theta_E/T) - 1\}] \qquad 3.35.3$$

$$C_V = 3R\{(\Theta_E/2T)/\sinh(\Theta_E/2T)\}^2 \qquad 3.35.4$$

where Θ_E is Einstein's characteristic temperature.

By comparing Debye's formulae with Einstein's we observe that the former contain integrals from zero to Θ_D where the latter contain merely simple functions of Θ_E. Thus Θ_E in a sense represents an average Θ covering the range from 0 to Θ_D. Thus at any given temperature the value of Θ_E which fits is always smaller than the value of Θ_D which fits.

If one tries to fit the experimental data by Einstein's formulae with a constant Θ_E one fails completely at the lowest temperatures, but at higher temperatures there is little to choose between Einstein's formulae and Debye's provided the value chosen for Θ_E is suitably adjusted. In fact when $T > \frac{1}{3}\Theta_D$ the values of $U_m - U_m^0$ calculated from Debye's formula do not differ appreciably from the values calculated from Einstein's formula provided one uses for Θ_E the value given by $\Theta_E = 0.73\Theta_D$. Similarly when $T > \frac{1}{3}\Theta_D$ the values of $S_m - S_m^0$ calculated from Debye's formula do not differ appreciably from the values calculated from Einstein's formula provided one takes $\Theta_E = 0.71\Theta_D$. The comparison is shown in table 3.7. The slight difference of about 2 % between the best values of Θ_E corresponding to a given Θ_D in the cases of the energy and the entropy is a measure of the accuracy lost by the substitution. Since the experimental data cannot be fitted exactly by a constant value of Θ_D considerable simplification can often be attained without significant loss of accuracy by using Einstein's formulae rather than Debye's provided one is concerned only with temperatures greater than $\frac{1}{3}\Theta_D$. At lower temperatures Debye's formulae should be used in preference to Einstein's.

TABLE 3.7

Comparison of Einstein's formulae with Debye's assuming
$\Theta_E = 0.73\Theta_D$ for energies
and $\Theta_E = 0.71\Theta_D$ for entropies

Θ_D/T	$(U_m - U_m^0)/3RT$		$(S_m - S_m^0)/3R$	
	Debye	Einstein	Debye	Einstein
0.1	0.964	0.963	3.64	3.64
0.2	0.929	0.929	2.945	2.95
0.4	0.860	0.861	2.26	2.26
0.6	0.794	0.797	1.85	1.86
0.8	0.733	0.736	1.575	1.58
1.0	0.675	0.679	1.36	1.37
1.2	0.620	0.625	1.19	1.19
1.4	0.571	0.575	1.045	1.045
1.6	0.525	0.527	0.925	0.925
1.8	0.482	0.483	0.825	0.820
2.0	0.442	0.442	0.735	0.730
2.2	0.405	0.403	0.657	0.650
2.4	0.371	0.368	0.590	0.580
2.6	0.339	0.334	0.529	0.518
2.8	0.310	0.304	0.476	0.463
3.0	0.284	0.276	0.429	0.414

§3.36 *Equilibrium between two phases*

Having discussed the thermodynamic properties of a single phase, we now turn to consider two phases in equilibrium. If we denote the two phases by superscripts $^{\alpha}$ and $^{\beta}$, the condition for equilibrium between the two phases is according to (1.39.5)

$$\mu^{\alpha}=\mu^{\beta} \qquad 3.36.1$$

or according to (3.15.6)

$$\lambda^{\alpha}=\lambda^{\beta}. \qquad 3.36.2$$

Since in any single phase of a pure substance the temperature T and pressure P may be varied independently and μ or λ may be regarded as a function of T, P, we may therefore regard (1) or (2) as expressing a relation between T and P for equilibrium between the two phases. It follows that when the two phases are in equilibrium, the temperature T and pressure P are not independently variable but either determines the other. We accordingly say that a single phase of one component has two degrees of freedom but a pair of phases of one component has only one degree of freedom.

§3.37 *Relation between temperature and pressure for two-phase equilibrium*

We now proceed to determine how the equilibrium pressure between two phases α and β depends on the temperature T. Differentiating (3.36.1) we have

$$\mathrm{d}\mu^{\alpha}=\mathrm{d}\mu^{\beta} \qquad 3.37.1$$

or

$$(\partial\mu^{\alpha}/\partial T)\mathrm{d}T+(\partial\mu^{\alpha}/\partial P)\mathrm{d}P=(\partial\mu^{\beta}/\partial T)\mathrm{d}T+(\partial\mu^{\beta}/\partial P)\mathrm{d}P. \qquad 3.37.2$$

Using (1.28.22) and (1.28.23), we obtain

$$(V_{\mathrm{m}}^{\beta}-V_{\mathrm{m}}^{\alpha})\mathrm{d}P=(S_{\mathrm{m}}^{\beta}-S_{\mathrm{m}}^{\alpha})\mathrm{d}T. \qquad 3.37.3$$

Formula (3) can also be obtained more directly from Maxwell's relation

$$(\partial P/\partial T)_V=(\partial S/\partial V)_T. \qquad 3.37.4$$

We apply this relation to a system consisting of the two phases α and β in equilibrium with each other. Since for this equilibrium to persist P is completely determined by T and is independent of V, we may replace the partial differential coefficient $(\partial P/\partial T)_V$ by $\mathrm{d}P/\mathrm{d}T$. Moreover at constant temperature and incidentally also constant pressure, S and V can only change through some amount of substance passing from the phase α to the phase β or conversely. Thus the ratio of the changes in S and in V is independent of the amount transferred from the one phase to the other. If then we denote by the symbol Δ the increase of any property when unit amount passes from the phase α to the phase β, we have

$$(\partial S/\partial V)_T = \Delta S/\Delta V \qquad 3.37.5$$

and so (4) becomes

$$\mathrm{d}P/\mathrm{d}T = \Delta S/\Delta V \qquad 3.37.6$$

which is formula (3) in different notation.

Since we may rewrite (3.36.1) as

$$H^\alpha_\mathrm{m} - TS^\alpha_\mathrm{m} = H^\beta_\mathrm{m} - TS^\beta_\mathrm{m} \qquad 3.37.7$$

it follows immediately that

$$T\Delta S = T(S^\beta_\mathrm{m} - S^\alpha_\mathrm{m}) = H^\beta_\mathrm{m} - H^\alpha_\mathrm{m} = \Delta H. \qquad 3.37.8$$

This relation has an obvious physical meaning, the same as that of (3.02.2). If unit amount passes isothermally from the phase α to the phase β, the heat q absorbed is equal to ΔH because the process occurs at constant pressure and it is also equal to $T\Delta S$ because, the system being in equilibrium throughout, the change is reversible.

If we now substitute from (8) into (6), we obtain

$$\mathrm{d}P/\mathrm{d}T = \Delta H/T\Delta V = (H^\beta_\mathrm{m} - H^\alpha_\mathrm{m})/T(V^\beta_\mathrm{m} - V^\alpha_\mathrm{m}) \qquad 3.37.9$$

which is known as *Clapeyron's relation.* This can also be obtained more directly by starting from

$$\mu^\alpha/T = \mu^\beta/T \qquad 3.37.10$$

instead of (3.36.1). Differentiating (10) we obtain

$$\{\partial(\mu^\alpha/T)/\partial T\}\mathrm{d}T + T^{-1}(\partial\mu^\alpha/\partial P)\mathrm{d}P = \{\partial(\mu^\beta/T)/\partial T\}\mathrm{d}T + T^{-1}(\partial\mu^\beta/\partial P)\mathrm{d}P \qquad 3.37.11$$

and so using (1.28.24) and (1.28.23)

$$-(H^\alpha_\mathrm{m}/T)\mathrm{d}T + (V^\alpha_\mathrm{m}/T)\mathrm{d}P = -(H^\beta_\mathrm{m}/T)\mathrm{d}T + (V^\beta_\mathrm{m}/T)\mathrm{d}P \qquad 3.37.12$$

whence (9) follows immediately. We have given these alternative derivations of (9) because of its great importance, as the prototype of other similar formulae in systems of more than one component.

§3.38 *Clapeyron's relation applied to two condensed phases*

Let us consider the application of Clapeyron's relation to the equilibrium between a solid and a liquid. Using the superscripts $^{\mathrm{S}}$ and $^{\mathrm{L}}$ to denote these two phases, we have for the variation of the equilibrium pressure with the equilibrium temperature according to (3.37.9)

$$\mathrm{d}P/\mathrm{d}T=(H_{\mathrm{m}}^{\mathrm{L}}-H_{\mathrm{m}}^{\mathrm{S}})/T(V_{\mathrm{m}}^{\mathrm{L}}-V_{\mathrm{m}}^{\mathrm{S}})=\Delta_{\mathrm{f}}H/T(V_{\mathrm{m}}^{\mathrm{L}}-V_{\mathrm{m}}^{\mathrm{S}})=\Delta_{\mathrm{f}}S/(V_{\mathrm{m}}^{\mathrm{L}}-V_{\mathrm{m}}^{\mathrm{S}}) \quad 3.38.1$$

where $\Delta_{\mathrm{f}}H$ is the proper enthalpy of fusion and $\Delta_{\mathrm{f}}S$ is the proper entropy of fusion. Since fusion is always an endothermic process, the numerator of (1) is always positive, but the denominator may have either sign. It is negative for water, but positive for most substances. Thus the melting point of ice is decreased by increase of pressure, but that of most solids is increased.

The application of Clapeyron's relation to the equilibrium between two solid phases is analogous. In (1) we need only make the superscript $^{\mathrm{L}}$ denote the phase stable at the higher temperature and $^{\mathrm{S}}$ the phase stable at the lower temperature, so that $H_{\mathrm{m}}^{\mathrm{L}}-H_{\mathrm{m}}^{\mathrm{S}}$ is positive. The sign of $\mathrm{d}P/\mathrm{d}T$ will then be the same as that of $V_{\mathrm{m}}^{\mathrm{L}}-V_{\mathrm{m}}^{\mathrm{S}}$.

For condensed phases, both $V_{\mathrm{m}}^{\mathrm{L}}$ and $V_{\mathrm{m}}^{\mathrm{S}}$ are small and their difference is much smaller. Usually a pressure of some hundred atmospheres is required to change the freezing point by a single degree. Let us take water as an illustrative example. We have

$$\begin{aligned}-\mathrm{d}P/\mathrm{d}T&=22\ \mathrm{J\ K^{-1}\ mole^{-1}}/(19.6-18.0)\ \mathrm{cm^3\ mole^{-1}}=22\ \mathrm{J\ K^{-1}}/1.6\ \mathrm{cm^3}\\&=220\ \mathrm{atm}/1.6\ \mathrm{K}=1.4\times10^2\ \mathrm{atm/K}.\end{aligned} \quad 3.38.2$$

As a second example, let us take sodium. We have

$$\begin{aligned}\mathrm{d}P/\mathrm{d}T&=7.1\ \mathrm{J\ K^{-1}\ mole^{-1}}/(24.6-24.2)\ \mathrm{cm^3\ mole^{-1}}=7.1\ \mathrm{J\ K^{-1}}/0.4\ \mathrm{cm^3}\\&=71\ \mathrm{atm}/0.4\ \mathrm{K}=1.8\times10^2\ \mathrm{atm/K}.\end{aligned} \quad 3.38.3$$

Hence as long as the pressure does not exceed a few atmospheres, the freezing point may for many purposes be regarded as unaffected by the pressure.

§3.39 *Clapeyron's relation applied to saturated vapour*

Let us now consider the equilibrium between a liquid and a gaseous phase. Using the superscripts $^{\mathrm{L}}$ for the liquid and $^{\mathrm{G}}$ for the gas we have according to (3.37.9)

$$\mathrm{d}P/\mathrm{d}T=(H_{\mathrm{m}}^{\mathrm{G}}-H_{\mathrm{m}}^{\mathrm{L}})/T(V_{\mathrm{m}}^{\mathrm{G}}-V_{\mathrm{m}}^{\mathrm{L}}). \quad 3.39.1$$

This exact relation can be transformed by making two approximations. In the first place we neglect the proper volume of the liquid compared with that of the vapour. In the second place we neglect the virial coefficients of the gas and treat it as perfect. With these approximations we have

$$V_m^G - V_m^L \approx RT/P \qquad 3.39.2$$

Substituting (2) into (1), we obtain

$$d \ln P/dT = (H_m^G - H_m^L)/RT^2 = \Delta_e H/RT^2 \qquad 3.39.3$$

where $\Delta_e H$ is the proper enthalpy of evaporation.

We denote equilibrium or saturated vapour pressure of a condensed phase by P_s and accordingly write in place of (3)

$$d \ln P_s/dT = \Delta_e H/RT^2 \qquad 3.39.4$$

or

$$d \ln P_s/d(1/T) = -\Delta_e H/R. \qquad 3.39.5$$

It follows from (5) that if we plot $\ln P_s$ against $1/T$ the curve so obtained has at each point a slope equal to $-\Delta H_e/R$. Actually $\Delta_e H$ varies so slowly with the temperature that this curve is nearly a straight line.

Formula (5) incidentally provides a method, rarely if ever mentioned, for determining the proper mass in the vapour. For by measuring P_s at several known temperatures we can use (5) to calculate $\Delta_e H$. We can then make direct calorimetric measurements to determine what mass of liquid is converted to vapour when a quantity of heat equal to $\Delta_e H$ is absorbed. This mass is then the proper mass of vapour.

The treatment of equilibrium between a solid and its vapour is precisely analogous. The saturated vapour pressure P_s of the solid is related to the temperature by

$$d \ln P_s/d(1/T) = -\Delta_s H/R \qquad 3.39.6$$

where $\Delta_s H$ is the proper enthalpy of sublimation.

§3.40 *Heat capacities of two phases in equilibrium*

Consider two phases of a single component in mutual equilibrium. Suppose now that we isolate unit amount of either of these phases and change its temperature, not at constant pressure, but adjusting the pressure to the value corresponding to two-phase equilibrium at each temperature. The quantity of heat absorbed in this phase will evidently, for a small temperature increase dT, be proportional to dT. We may therefore write for either of the two phases

$$q = C_{eq} dT. \qquad 3.40.1$$

C_{eq} is the heat capacity at two-phase equilibrium. Since moreover the change is reversible we may write instead of (1)

$$dS_m = C_{eq} dT/T. \qquad 3.40.2$$

But for the change in question

$$\mathrm{d}S_{\mathrm{m}}=\{(\partial S_{\mathrm{m}}/\partial T)_P+(\partial S_{\mathrm{m}}/\partial P)_T\,\mathrm{d}P/\mathrm{d}T\}\mathrm{d}T. \qquad 3.40.3$$

Comparing (2) with (3) we see that

$$C_{\mathrm{eq}}=T\{(\partial S_{\mathrm{m}}/\partial T)_P+(\partial S_{\mathrm{m}}/\partial P)\mathrm{d}P/\mathrm{d}T\}=C_P-\alpha V_{\mathrm{m}}T\,\mathrm{d}P/\mathrm{d}T \qquad 3.40.4$$

using the definition (3.03.2) of C_P and Maxwell's relation (1.47.4). Now substituting from (3.37.9) into (4) we obtain

$$C_{\mathrm{eq}}=C_P-\alpha V_{\mathrm{m}}\Delta H/\Delta V \qquad 3.40.5$$

where Δ denotes the increase when unit amount passes isothermally from the one phase to the other; as regards sign the same convention must of course be used for ΔH and ΔV.

§3.41 *Heat capacities at saturation*

The most important application of the formulae of the previous section is to the equilibrium between a liquid and its vapour. The quantities C_{eq} are then called the heat capacities at saturation and are denoted by C_{sat}. If we neglect the second virial coefficient of the gas and also neglect the proper volume of the liquid compared with that of the gas, formula (3.40.5) becomes

$$C_{\mathrm{sat}}=C_P-\alpha\Delta_{\mathrm{e}}H\,PV_{\mathrm{m}}/RT \qquad 3.41.1$$

where $\Delta_{\mathrm{e}}H$ is the proper enthalpy of evaporation.

Formula (1) is applicable either to the vapour or to the liquid, but the importance of the second term on the right is very different in the two cases. For the vapour we have, still neglecting the second virial coefficient,

$$\alpha=T^{-1} \qquad PV_{\mathrm{m}}=RT \qquad 3.41.2$$

so that, using the superscript $^{\mathrm{G}}$ for the gas, we obtain

$$C_{\mathrm{sat}}^{\mathrm{G}}=C_P^{\mathrm{G}}-\Delta_{\mathrm{e}}H/T=C_P^{\mathrm{G}}-\Delta_{\mathrm{e}}S. \qquad 3.41.3$$

The second term on the right may be numerically greater than the first, in which case $C_{\mathrm{sat}}^{\mathrm{G}}$ is negative. For example for steam at its normal boiling point

$$C_P=34\ \mathrm{J\ K^{-1}\ mole^{-1}}$$

$$\Delta_{\mathrm{e}}S=\Delta_{\mathrm{e}}H/T=40.6\ \mathrm{kJ\ mole^{-1}}/373\ \mathrm{K}=109\ \mathrm{J\ K^{-1}\ mole^{-1}}$$

so that

$$C_{\mathrm{sat}}^{\mathrm{G}}=(34-109)\ \mathrm{J\ K^{-1}\ mole^{-1}}=-75\ \mathrm{J\ K^{-1}\ mole^{-1}}$$

and we see that the heat capacity of steam at saturation is negative.

For the liquid phase on the other hand the second term on the right of (1) is much smaller than for the gas because V_m is smaller by a factor of something like 10^{-3} or less. Consequently for the liquid phase we may neglect this term and replace (1) by

$$C_{\mathrm{sat}}^{\mathrm{L}} = C_P^{\mathrm{L}} \qquad 3.41.4$$

where the superscript $^{\mathrm{L}}$ denotes the liquid phase.

The formulae of this section may also be applied to the equilibrium conditions between solid and vapour. Formula (3) is then applicable to the vapour and formula (4) to the solid.

§3.42 *Temperature dependence of enthalpies of evaporation and of fusion*

Consider any phase change such as evaporation or fusion and let the symbol Δ denote the increase in any property when unit amount passes isothermally from the one phase to the other in the direction such that ΔH is positive, i.e. from liquid to gas or from solid to liquid. Then we have

$$\Delta H/T = \Delta S. \qquad 3.42.1$$

Differentiating with respect to T, varying P so as to maintain equilibrium, we have

$$\mathrm{d}(\Delta H/T) = \mathrm{d}(\Delta S)/\mathrm{d}T = \Delta(\mathrm{d}S/\mathrm{d}T) = \Delta C_{\mathrm{eq}}/T \qquad 3.42.2$$

or

$$\mathrm{d}(\Delta H)/\mathrm{d}T - \Delta H/T = \Delta C_{\mathrm{eq}}. \qquad 3.42.3$$

For equilibrium between liquid and vapour, $C_{\mathrm{eq}} = C_{\mathrm{sat}}$ is given by (3.41.3) for the vapour and by (3.41.4) for the liquid. Substituting these into (3) we obtain

$$\mathrm{d}(\Delta_{\mathrm{e}} H)/\mathrm{d}T = C_P^{\mathrm{G}} - C_P^{\mathrm{L}} \qquad 3.42.4$$

the terms $\Delta_{\mathrm{e}} H/T$ on either side cancelling. Formula (4) involves the several approximations mentioned in §3.41. It is formally similar to the exact formula for a process taking place between pressure limits independent of the temperature.

To obtain the temperature coefficient of an enthalpy of fusion, we have to go back to (3.40.5), which we rewrite in the form

$$C_{\mathrm{eq}} = C_P - (\partial V_{\mathrm{m}}/\partial T)_P(\Delta_{\mathrm{f}} H/\Delta_{\mathrm{f}} V) \qquad 3.42.5$$

where Δ_{f} denotes the increase of a proper quantity on fusion. Substituting

(5) into (3), we obtain

$$\mathrm{d}(\Delta_{\mathrm{f}}H)/\mathrm{d}T = \Delta_{\mathrm{f}}C_P + \Delta_{\mathrm{f}}H/T - (\Delta_{\mathrm{f}}H/T)(\partial \ln \Delta_{\mathrm{f}}V/\partial \ln T)_P \qquad 3.42.6$$

a formula due to Planck*. The magnitude of the last term on the right is usually unknown and it is often neglected. Formula (6) then reduces to

$$\mathrm{d}(\Delta_{\mathrm{f}}H)/\mathrm{d}T = \Delta_{\mathrm{f}}C_P + \Delta_{\mathrm{f}}H/T. \qquad 3.42.7$$

Of the two terms on the right, either may be numerically greater. We thus have a formula not even approximately of the same form as the formula for a process taking place between pressure limits independent of the temperature.

Evidently the formulae of this section may mutatis mutandis be applied to the equilibrium between two solid phases.

§3.43 *Triple point*

We have seen that the equilibrium condition for a single component between two phases α and β

$$\mu^{\alpha}(T, P) = \mu^{\beta}(T, P) \qquad 3.43.1$$

is equivalent to a relation between P and T which can be represented by a curve on a P–T diagram. Similarly the equilibrium between the phases α and γ can be represented by a curve on a P–T diagram. If these two curves cut, we shall have at the point of intersection

$$\mu^{\alpha}(T, P) = \mu^{\beta}(T, P) = \mu^{\gamma}(T, P) \qquad 3.43.2$$

and the three phases α, β, γ will be in mutual equilibrium. This point of intersection is called a *triple point* and the values of T and P at the triple point are called the *triple-point temperature* and the *triple-point pressure*.

We have seen that a single component in one phase has two degrees of freedom since temperature and pressure can be varied independently and that two phases in mutual equilibrium have only one degree of freedom since temperature and pressure are mutually dependent. We now see that three phases can exist in mutual equilibrium only at a particular temperature and particular pressure. Thus three phases of a single component in mutual equilibrium have no degree of freedom.

In figure 3.4 the conditions of mutual equilibrium for H_2O are shown† on the P–T diagram.

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* Planck, Ann. Phys. Lpz. 1887 **30** 574.

† From Landolt–Börnstein Tables.

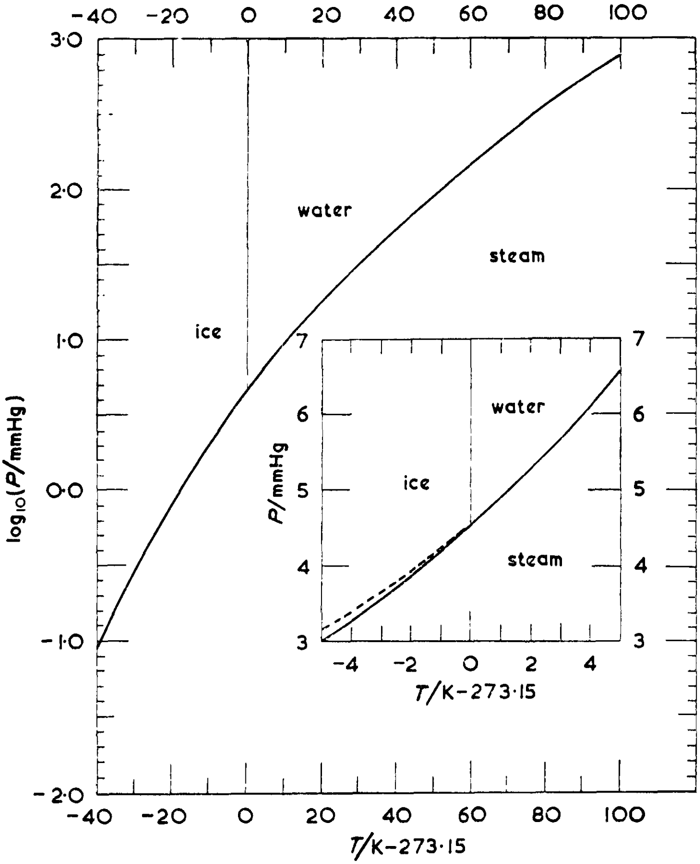

Fig. 3.4. Equilibrium between ice, water, and steam

Triple points can also exist for two solid phases and one liquid phase or for two solid phases and a vapour phase or for three solid phases. More rarely we may have two liquid phases and a vapour phase or a solid phase. A triple point can occur in a region where all three phases are metastable. The conditions of equilibrium for sulphur are shown* in figure 3.5. There are three stable triple points

T_1: equilibrium between monoclinic, liquid, and vapour
T_2: equilibrium between rhombic, monoclinic, and liquid
T_3: equilibrium between rhombic, monoclinic, and vapour

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* From Landolt–Börnstein Tables.

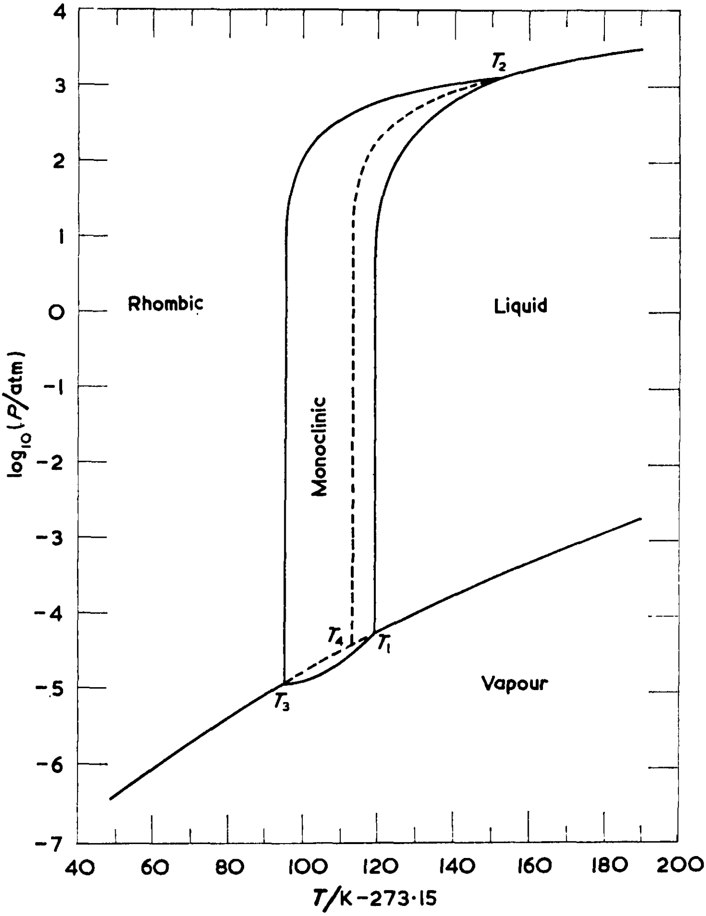

Fig. 3.5. Phase equilibria of sulphur

and one metastable triple point

T_4: equilibrium between rhombic, liquid, and vapour, all three phases being metastable and the monoclinic being the stable form.

§3.44 *Critical points*

The P–V_m isotherms of all pure substances fall into two classes according as the temperature lies above or below a *critical temperature* T_c. Examples of each class are shown in figure 3.6 for carbon dioxide* and in figure 3.7 for xenon†.

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* Michels, Blaisse, and Michels, Proc. Roy. Soc. A 1937 **160** 367.

† Habgood and Schneider, Can. J. Chem. 1954 **32** 98.

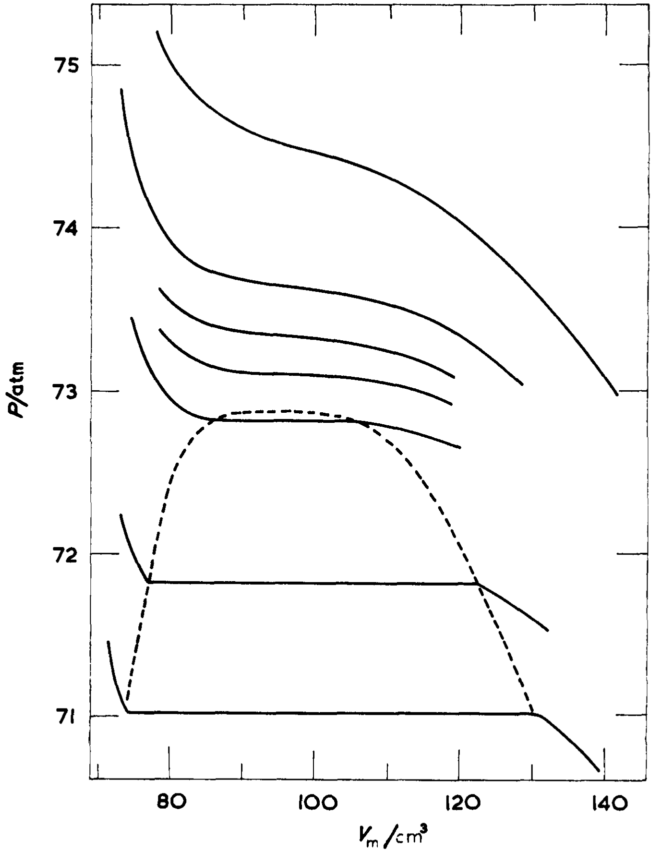

Fig. 3.6. Isotherms of carbon dioxide

When the proper volume is sufficiently large both classes approximate to the rectangular hyperbolae $PV_m = RT$ of a perfect gas. As the proper volume diminishes, the form of the two classes is quite different. At temperatures greater than the critical, there is a smooth regular variation along the whole isotherm, which can be expressed mathematically by saying that it is a single analytic curve or expressed physically by saying that throughout the isotherm there is a single fluid phase. At temperatures below the critical on the other hand, the isotherm consists of three analytically distinct parts separated by discontinuities of the slope. The middle portion is a straight line parallel to the V_m axis. These parts represent respectively the pure gas, the saturated vapour in equilibrium with the liquid, and the pure liquid. The isothermal curve for the critical temperature T_c is the borderline between

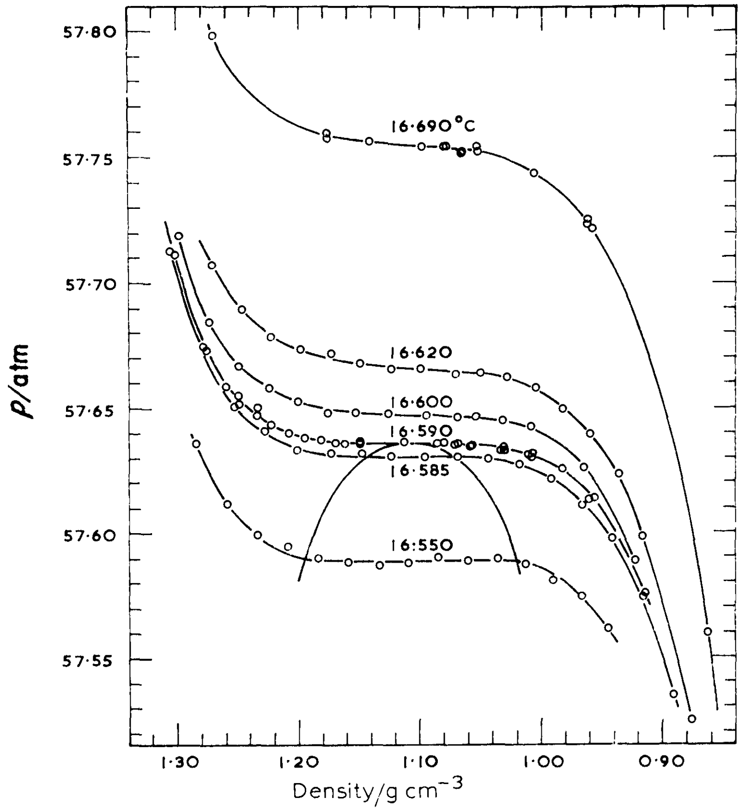

Fig. 3.7. Pressure–density isotherms of xenon in the immediate neighbourhood of the critical temperature

the two classes of isotherms. In this isotherm the horizontal portion is reduced to a single point of horizontal inflexion.

Both diagrams show the locus of the points representing on the left the liquid phase under the pressure of its vapour and on the right the locus of the points representing the saturated vapour. As the temperature increases the proper volume of the liquid at the pressure of its vapour increases, while the proper volume of the saturated vapour decreases. At the critical temperature the isotherm has a point of horizontal inflexion where the liquid and vapour phases cease to be distinguishable. The state represented by this point is called the *critical state*; the pressure and proper volume in the critical state are called the *critical pressure* P_c and the *critical volume* V_c respectively.

To recapitulate, above the critical temperature the substance can exist in only one fluid state. Below the critical temperature it can exist in two states, the liquid with a proper volume less than the critical volume and the gas with a proper volume greater than the critical volume. The equilibrium pressure between the two phases, liquid and vapour, can have values up to but not exceeding the critical pressure.

§3.45 *Continuity of state*

The relation between pressure P and proper volume V_m of a single component at a temperature below the critical temperature is shown diagrammatically in figure 3.8. The portion KL represents the liquid state, the portion VW the gaseous state, and the straight portion LV the two-phase system liquid + saturated vapour.

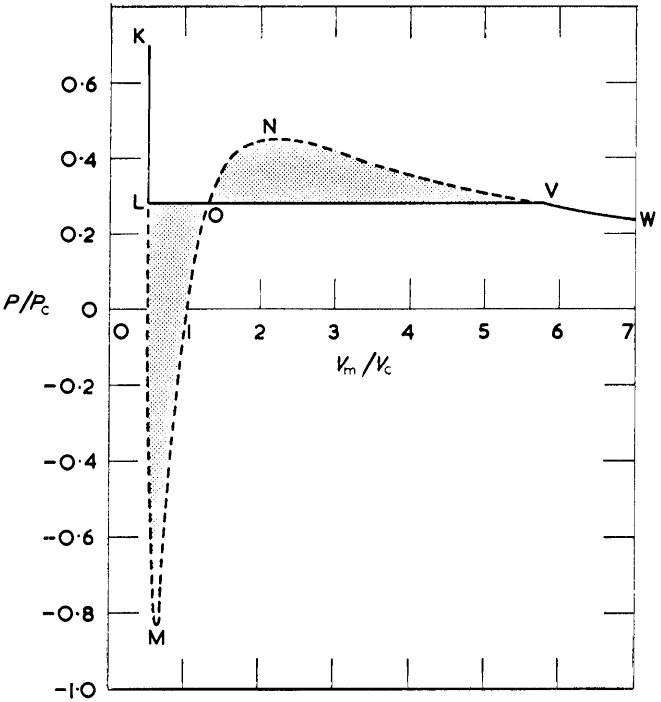

Fig. 3.8. Continuity between liquid and gas phases

At the given temperature the substance can be brought from the liquid state to the gaseous state, or conversely, only by a change during part of which two separate phases will be present. By varying the temperature, however, it is possible to bring the substance from the gaseous state represented by W to the liquid state represented by K by a continuous change throughout which there is never more than one phase present. It is only necessary to raise the temperature above the critical temperature, keeping the volume sufficiently greater than the critical volume, then compress the fluid to a volume below the critical volume, keeping the temperature above the critical temperature, and finally cool the liquid to its original temperature, keeping the volume sufficiently below the critical volume. This possibility of continuity between the liquid and gaseous states was first realized by James Thomson*, and he suggested that the portions KL and VW of the isotherm are actually parts of one smooth curve, such as KLMONVW. In point of fact, states corresponding to the portion VN are realizable as supersaturated vapour, and under certain circumstances the same may be true of the portion LM representing superheated liquid. Each of these portions represents states stable with respect to infinitesimal variations, but metastable relative to the two-phase system liquid+saturated vapour. The portion of the curve MON, on the other hand, represents states absolutely unstable, since here

$$(\partial V_{\mathrm{m}}/\partial P)_T > 0 \qquad 3.45.1$$

and, according to (1.38.4), such states are never realizable.

Although the states represented by points on the curve LMONV are either metastable or unstable, they have been treated† as equilibrium states. It follows that the sequence of states represented by the curve LMONV corresponds to a reversible process. The change in the chemical potential μ of the fluid in passing through this sequence of states is, according to (1.28.23) given by

$$\mu^{\mathrm{G}} - \mu^{\mathrm{L}} = \int_{\mathrm{L}}^{\mathrm{G}} (\partial\mu/\partial P)_T \mathrm{d}P = \int_{\mathrm{L}}^{\mathrm{G}} V_{\mathrm{m}} \mathrm{d}P \qquad 3.45.2$$

where the integrals are to be evaluated along the curve LMONV. But, since the two states represented by $^{\mathrm{L}}$ and $^{\mathrm{G}}$ can exist in equilibrium with each other, we have

$$\mu^{\mathrm{G}} = \mu^{\mathrm{L}}. \qquad 3.45.3$$

From (2) and (3) we deduce

$$\int_{\mathrm{L}}^{\mathrm{G}} V_{\mathrm{m}} \mathrm{d}P = 0 \qquad 3.45.4$$

where the integral is to be evaluated along the curve LMONV. The geo-

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* J. Thomson, Proc. Roy. Soc. 1871 **20** 1.

† Maxwell, Nature 1875 **11** 357.

metrical significance of (4) is that the two shaded surfaces LMO and ONV are of equal area. This condition is due to Maxwell*.

It is instructive to reconsider continuity of state in terms of the Helmholtz function $\mathcal{A}\!\!F$. Imagine this to be plotted as vertical coordinate against T and V as horizontal Cartesian coordinates. The resulting locus is a curved surface. Consider now cross-sections of this surface by planes T=const. Examples of these are shown diagrammatically in figure 3.9 and since

$$(\partial \mathcal{A}\!\!F/\partial V)_T = -P \qquad 3.45.5$$

the slope of each curve at each point is equal to $-P$.

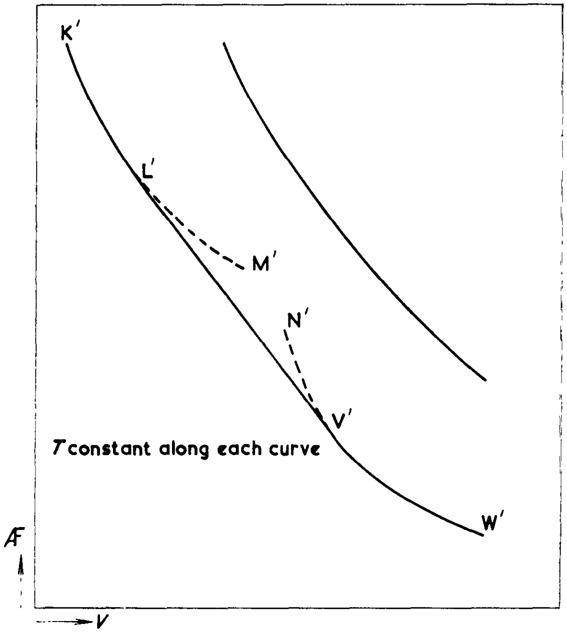

Fig. 3.9. Stable and metastable isotherms

In the upper curve we see that as V increases, the negative slope steadily decreases numerically and so P decreases steadily. This is typical of any temperature above the critical.

In the lower curve we see that there are two portions K′L′ and V′W′ in which the negative slope decreases steadily as V increases and these are joined by a straight line L′V′ touching K′L′ at L′ and touching V′W′ at V′. These three portions correspond to liquid, to gas, and to a two-phase liquid–vapour system. This is typical of a temperature below the critical. The

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* Maxwell, Nature 1875 **11** 357.

broken portion of curve L′M′ represents superheated liquid and the broken portion V′N′ represents supersaturated vapour. We see immediately that all states represented by these portions of curve are metastable, for any point on either of them lies above a point of the same volume V on the straight line L′V′. This means that the Helmholtz function of the superheated liquid or supersaturated vapour is greater than in a system of the same volume consisting of a mixture of liquid L′ and saturated vapour V′.

The portions of curve L′M′ and N′V′ have curvature concave upwards so that

$$\partial P/\partial V = -\partial^2 \mathcal{A}/\partial V^2 < 0. \tag{3.45.6}$$

Hence according to (1.38.4) they represent states internally stable, though metastable with respect to a two-phase mixture. If however we wish to unite these two portions into a single smooth curve, the middle portion would necessarily have a curvature concave downwards. This would correspond to a positive value of $\partial P/\partial V$ and so to unstable states and we saw in §1.38 that such states are never realizable. It may therefore be argued that no physical significance could be attached to this part of the curve. Nevertheless, if the realizable parts K′L′M′ and N′V′W′ of the surface could be represented by the same analytical function, it would be reasonable from a mathematical point of view to consider the complete surface. Having constructed such a surface and considering a section corresponding to a particular temperature below the critical, we could then plot $P = -\partial \mathcal{A}/\partial V$ against V and so construct a curve such as that in figure 3.8. From this construction it follows of necessity that in figure 3.8 the area below the broken curve LMONV and the area below the straight line LV are both equal to the height of L′ above V′ in figure 3.9. Consequently these two areas are equal. From this it follows immediately that the two shaded areas are equal as already proved. Since the portion MON of the curve cannot be realized experimentally, instead of saying that the two-phase equilibrium is determined by the condition of equality of the two shaded areas, it is perhaps more correct to say that, L and V being known, if the connecting portion of the curve were sketched in such a manner as to make the two shaded areas unequal it would be nonsensical for then $-P$ would not be the slope of any conceivable curve in the plot of $\mathcal{A}$ against V.

§3.46 *Two phases at different pressures*

In our previous considerations of equilibrium between two phases of one component, we have assumed the equilibrium to be complete so that the two phases were at the same pressure. The distribution equilibrium of one component between two phases at different pressures is also of interest. Let us denote the two phases by the superscripts $^{\alpha}$ and $^{\beta}$. Then the equilibrium condition determining the change from the one phase to the other is according to (1.42.1)

$$\mu^{\alpha}=\mu^{\beta}. \tag{3.46.1}$$

If we vary the common temperature T of the two phases and the pressures P^{α} and P^{β} of the two phases, the condition for maintenance of equilibrium is

$$\mathrm{d}\mu^{\alpha}=\mathrm{d}\mu^{\beta} \tag{3.46.2}$$

or

$$(\partial\mu^{\alpha}/\partial T)\mathrm{d}T+(\partial\mu^{\alpha}/\partial P^{\alpha})\mathrm{d}P^{\alpha}=(\partial\mu^{\beta}/\partial T)\mathrm{d}T+(\partial\mu^{\beta}/\partial P^{\beta})\mathrm{d}P^{\beta}. \tag{3.46.3}$$

Substituting from (1.28.22) and (1.28.23) we obtain

$$-S_{\mathrm{m}}^{\alpha}\mathrm{d}T+V_{\mathrm{m}}^{\alpha}\mathrm{d}P^{\alpha}=-S_{\mathrm{m}}^{\beta}\mathrm{d}T+V_{\mathrm{m}}^{\beta}\mathrm{d}P^{\beta} \tag{3.46.4}$$

or

$$V_{\mathrm{m}}^{\beta}\mathrm{d}P^{\beta}-V_{\mathrm{m}}^{\alpha}\mathrm{d}P^{\alpha}=(S_{\mathrm{m}}^{\beta}-S_{\mathrm{m}}^{\alpha})\mathrm{d}T=\underset{\alpha\to\beta}{\Delta}S\mathrm{d}T \tag{3.46.5}$$

where $\Delta_{\alpha\to\beta}$ is used to denote the increase of a quantity when unit amount passes from the phase α to the phase β.

Since we may rewrite (1) as

$$H_{\mathrm{m}}^{\alpha}-TS_{\mathrm{m}}^{\alpha}=H_{\mathrm{m}}^{\beta}-TS_{\mathrm{m}}^{\beta} \tag{3.46.6}$$

it follows immediately that

$$T\underset{\alpha\to\beta}{\Delta}S=\underset{\alpha\to\beta}{\Delta}H \tag{3.46.7}$$

just as for two phases at the same pressure. In fact formula (3.37.8) is a special example of (7) and the physical significance is the same in both cases.

If we now substitute from (7) into (5) we obtain

$$V_{\mathrm{m}}^{\beta}\mathrm{d}P^{\beta}-V_{\mathrm{m}}^{\alpha}\mathrm{d}P^{\alpha}=\underset{\alpha\to\beta}{\Delta}H\mathrm{d}T/T. \tag{3.46.8}$$

It is evident that two of the three quantities T, P^{α}, P^{β} are independent and so the system has two degrees of freedom. The most important application of these formulae is to the equilibrium between a liquid and its vapour. We then use the superscript $^{\mathrm{L}}$ for the liquid and $^{\mathrm{G}}$ for the vapour. In this notation (8) becomes

$$V_{\mathrm{m}}^{\mathrm{G}}\mathrm{d}P^{\mathrm{G}}-V_{\mathrm{m}}^{\mathrm{L}}\mathrm{d}P^{\mathrm{L}}=(\Delta_{\mathrm{e}}H/T)\mathrm{d}T \tag{3.46.9}$$

where $\Delta_{\mathrm{e}}H$ is the proper enthalpy of evaporation. According to the definition

(3.17.1) of fugacity p, we may replace (9) by

$$RT\,\mathrm{d}\ln p - V_{\mathrm{m}}^{\mathrm{L}}\mathrm{d}P^{\mathrm{L}} = (\Delta_{\mathrm{e}}H/T)\mathrm{d}T. \qquad 3.46.10$$

In particular at constant temperature we have for the dependence of the fugacity of the gas on the external pressure P on the liquid

$$\mathrm{d}\ln p/\mathrm{d}P = V_{\mathrm{m}}^{\mathrm{L}}/RT \qquad (T\ \text{const.}). \qquad 3.46.11$$

If we treat the vapour as a perfect gas, we may replace p by P^{G}.

If, on the other hand, we maintain constant the pressure P on the liquid, we obtain from (10) for the dependence of the gas fugacity on the temperature

$$\mathrm{d}\ln p/\mathrm{d}T = \Delta_{\mathrm{e}}H/RT^2 \qquad (P\ \text{const.}) \qquad 3.46.12$$

or if we treat the vapour as a perfect gas

$$\mathrm{d}\ln P^{\mathrm{G}}/\mathrm{d}T = \Delta_{\mathrm{e}}H/RT^2 \qquad 3.46.13$$

or

$$\mathrm{d}\ln P^{\mathrm{G}}/\mathrm{d}(1/T) = -\Delta_{\mathrm{e}}H/R. \qquad 3.46.14$$

It is instructive to compare (14) with (3.39.5). The latter involves neglecting the proper volume of the liquid compared with that of the vapour, but the former involves no such approximation. The difference between the exact formula (14) and the approximate formula (3.39.5) is usually negligible owing to the fact that in order to affect the saturated vapour pressure P_{s} appreciably by change of the hydrostatic pressure P^{L} at constant temperature, one requires according to (11) pressures considerably greater than the vapour pressure itself.

The direct experimental application of these formulae would require the separation of the liquid from the vapour by a membrane permeable to the vapour, but not to the liquid. This is difficult to achieve, though not impossible. Consequently the formulae have not much direct practical application. They have nevertheless a real importance, which will become clear when we consider systems of two or more components. We shall find that these formulae remain true in the presence of another component gas insoluble in the liquid, provided we interpret P^{G} as the partial pressure of the vapour when mixed with the inert gas. We cannot profitably say more at this stage, but we shall return to this point in §4.13.

§3.47 *Fugacity of a condensed phase*

In §3.17 we defined the fugacity p of a gaseous pure substance in terms of its absolute activity λ. We now define the *fugacity of a pure substance* in any condensed phase as being equal to the fugacity in the gas phase with which it is in equilibrium. Evidently when two condensed phases are in equilibrium with each other the fugacities must be equal in the two phases.

With this extended definition we may regard formula (3.46.10), namely

$$\mathrm{d}\ln p=(\Delta_e H/RT^2)\mathrm{d}T+(V_\mathrm{m}^\mathrm{L}/RT)\mathrm{d}P \qquad 3.47.1$$

as expressing the dependence of p, the *fugacity of a liquid*, on the temperature T and the external pressure P. A precisely analogous relation applies to a solid.

§3.48 *Corresponding states of fluids*

The principle of *corresponding states* asserts that for a group of similar substances the equation of state can be written in the form

$$P/P_\mathrm{c}=\phi\{(T/T_\mathrm{c}),(V_\mathrm{m}/V_\mathrm{c})\} \qquad 3.48.1$$

where ϕ is the same function for all the substances of the group.

Whereas it is not possible to express the equation of state in any simple analytical form, the principle of corresponding states is obeyed with a useful degree of accuracy by a considerable number of substances. It is in fact obeyed within the accuracy of experiment by the three inert elements Ar, Kr, Xe and to a high degree of accuracy by these substances together with Ne, N_2, O_2, CO, and CH_4. It would be misleading to try to divide substances sharply into two groups, those which do and those which do not obey the principle. It is obeyed more or less accurately by a great variety of substances. Deviations occur due to any one or several of the following causes:

(a) quantal effects in the lightest molecules, especially H_2, He, and to a much smaller extent Ne;

(b) polarity of the molecule or presence of strong polar groups even though the resultant dipole moment vanishes as in CO_2, SF_6;

(c) large departures of shape from rough spherical symmetry as in the higher alkanes and alkenes.

The principle is not obeyed at all by substances whose molecules form hydrogen bonds, especially those containing hydroxyl or amino groups, nor those such as NO_2 whose molecules associate.

We shall now review* briefly some of the experimental data which show directly or indirectly how well certain substances especially Ne, Ar, Kr, Xe, N_2, O_2, CO, CH_4 obey an equation of state of the common form (1).

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* Guggenheim, J. Chem. Phys. 1945 **13** 253; cf. Pitzer, J. Chem. Phys. 1939 **7** 583.

TABLE 3.8

Corresponding states of gases and liquids

	Formula	Ne	Ar	Kr	Xe	N_2	O_2	CO	CH_4
1	$M/\mathrm{g\ mole}^{-1}$	20.18	39.94	83.7	131.3	28.02	32.00	28.00	16.03
2	T_c/K	44.8	150.7	209.4	289.8	126.0	154.3	133.0	190.3
3	$V_c/\mathrm{cm^3\ mole}^{-1}$	41.7	75.3	92.1	118.8	90.2	74.5	93.2	98.8
4	P_c/atm	26.9	48.0	54.1	57.6	33.5	49.7	34.5	45.7
5	P_cV_c/RT_c	0.305	0.292	0.290	0.288	0.292	0.292	0.294	0.289
6	T_B/K	121	411.5			327		345	491
7	T_B/T_c	2.70	2.73			2.59		2.6	2.58
8	$T_s/\mathrm{K}\ (P_s=P_c/50)$	25.2	86.9	122.0	167.9	74.1	90.1	78.9	110.5
9	T_s/T_c	0.563	0.577	0.582	0.580	0.588	0.583	0.593	0.581
10	$\Delta_eH/R\ \mathrm{K}$	224	785	1086	1520	671	820	727	1023
11	Δ_eH/RT_s	8.9	9.04	8.91	9.06	9.06	9.11	9.22	9.26
12	$V_m/\mathrm{cm^3\ mole}^{-1}$		228.1	34.1	42.7				
13	V_m/V_c		0.374	0.371	0.376				

In table 3.8 the first row gives the proper mass M, the next three rows the critical temperature T_c, critical volume V_c, and critical pressure P_c. The fifth row gives values of P_cV_c/RT_c which according to the principle should have a universal value. All the values lie close to 0.29. It is of interest to note that the value for xenon based on recent measurements is closer to 0.29 than the best experimental value 0.278 quoted in 1945.

In figure 3.10 the experimental data on the second virial coefficients of Ar, Kr, Xe, and CH_4 are shown in the form of B/V_c plotted against T/T_c. The data for the four substances were shown by McGlashan and Potter* to be well fitted from high values of T/T_c down to $T/T_c=0.6$ by the empirical formula

$$B/V_c=0.430-0.886(T_c/T)-0.694(T_c/T)^2. \qquad 3.48.2$$

They are also well fitted from high values of T/T_c down to 0.5 by the curve in figure 3.10 which represents the formula†

$$B/V_c=0.440+1.40\{1-\exp(0.75T_c/T)\} \qquad 3.48.3$$

which can be derived theoretically from an interaction energy w between a pair of molecules distant r apart of the 'square-well' form given by

$$\begin{aligned} r&<\sigma & w&=\infty \\ \sigma<r&<1.5\sigma & w&=-\varepsilon \qquad 3.48.4 \\ r&>1.5\sigma & w&=0 \end{aligned}$$

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* McGlashan and Potter, Proc. Roy. Soc. A 1962 **267** 478.

† Guggenheim, Applications of Statistical Mechanics, Clarendon Press 1966 p. 36.

when the parameters σ and ε have the values given by

$$\tfrac{2}{3}\pi L\sigma^3 = 0.447 V_c \qquad \varepsilon = 0.936kT_c. \qquad 3.48.5$$

The Boyle temperature T_B at which the second virial coefficient changes sign is given in the sixth row of table 3.8. In the seventh row are given values of T_B/T_c and all these values lie near 2.7.

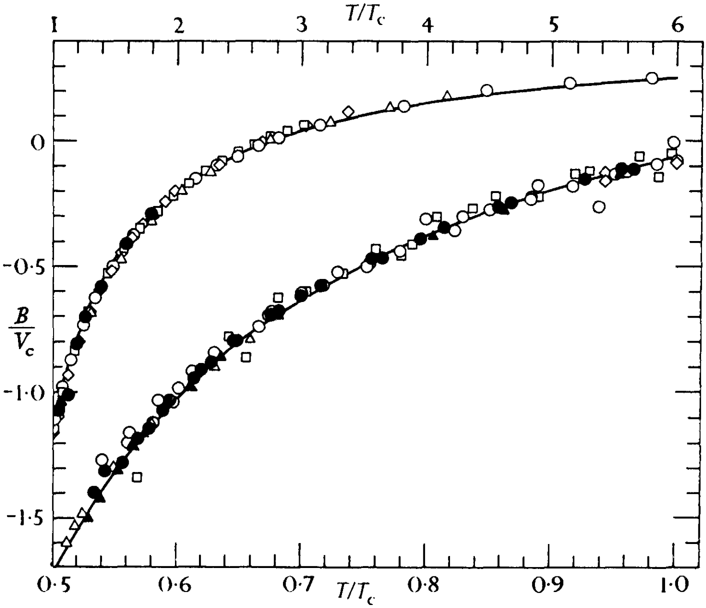

Fig. 3.10. Reduced second virial coefficients
The left-hand and upper scales relate to the upper curve.
The right-hand and lower scales relate to the lower curve.
○●, Ar; △▲, Kr; ◇, Xe; □, CH$_4$.

● Recent measurements communicated privately to the author by Rowlinson and by Staveley.

▲ Recent measurements communicated privately to the author by Rowlinson.

If ϱ^L denotes the density of the liquid and ϱ^G that of the vapour in mutual equilibrium at the temperature T, while ϱ_c denotes the density at the critical point, then according to the principle of corresponding states we should expect ϱ^L/ϱ_c and ϱ^G/ϱ_c to be common functions of T/T_c. How nearly this is the case is shown in figure 3.11. The curve in the diagram is drawn according to the empirical formulae

$$(\varrho^L + \varrho^G)/2\varrho_c = 1 + \tfrac{3}{4}(1 - T/T_c) \qquad 3.48.6$$

$$(\varrho^L - \varrho^G)/\varrho_c = \tfrac{7}{2}(1 - T/T_c)^{\frac{1}{3}}. \qquad 3.48.7$$

It is a pure accident that the data can be represented by formulae with such simple numerical coefficients. These formulae as displayed above are of high relative accuracy, but if used to compute ϱ^G the percentage inaccuracy increases with decrease of temperature and becomes serious below $T \approx 0.65 T_c$. It is therefore not recommended to use these formulae for computing values of ϱ^G. There are however occasions when we require relatively accurate

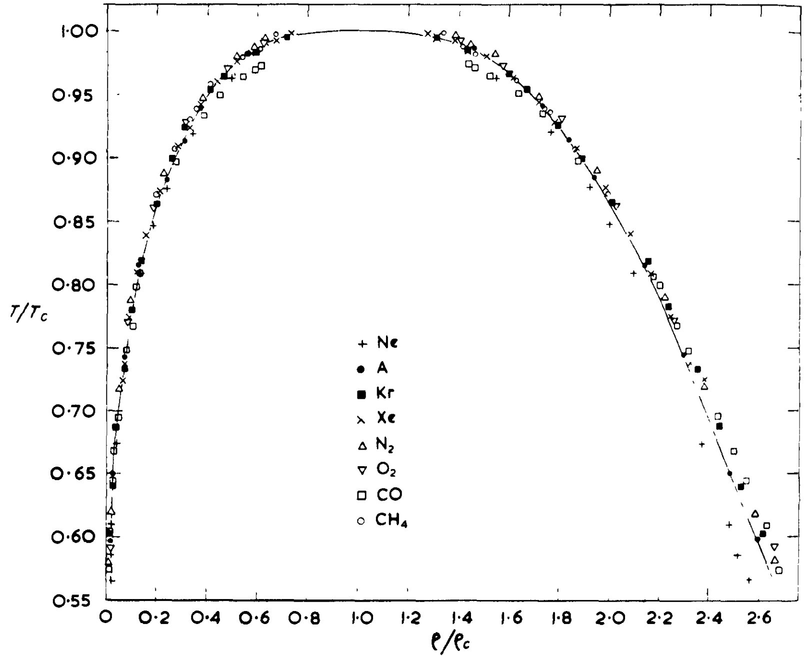

Fig. 3.11. Reduced densities of coexisting liquid and gas phases

values, not of ϱ^G itself, but of $(\varrho^L - \varrho^G)/\varrho_c$; on such occasions formula (9) in view of its extreme simplicity and surprisingly high accuracy, has much to recommend it. An example of its use will occur in §3.65.

At temperatures considerably below the critical temperature say $T < 0.65 T_c$, it is more useful to consider the saturated vapour pressure P_s instead of ϱ^G. According to the principle of corresponding states we should expect P_s/P_c to be a common function of T/T_c. That this is approximately the case is seen from figure 3.12, where $\ln(P_s/P_c)$ is plotted against T_c/T for several substances. It is clear that the relation is nearly linear, so that we may write

$$\ln(P_s/P_c) = A - BT_c/T \qquad 3.48.8$$

where A, B are constants having nearly the same values for the several substances. In the diagram the straight line which best fits the data for argon, krypton, and xenon has been drawn. For this line

$$A=5.29 \qquad B=5.31 \qquad \text{(triple point to critical point).} \tag{3.48.9}$$

The fact that A is nearly but not exactly equal to B, means that the straight line goes near to but not through the critical point. A formula of the type (8) has a theoretical basis at low temperatures, where the vapour does not differ significantly from a perfect gas and the proper enthalpy of evaporation is nearly independent of the temperature. Under these conditions $\Delta_e H/R = BT_c$. At higher temperatures where the vapour pressure is greater, neither of these conditions holds; the vapour deviates appreciably from a perfect gas and $\Delta_e H$ decreases, becoming zero at $T=T_c$. At such temperatures formula (8) is empirical, but remains surprisingly accurate owing to a compensation between the two deviations.

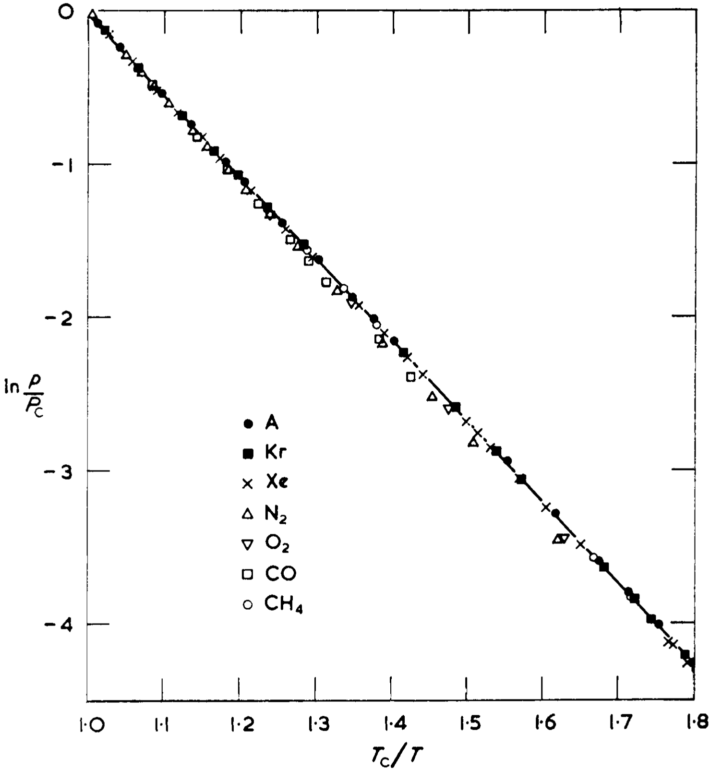

Fig. 3.12. Relation between vapour pressure and temperature

In the temperature range between the triple point and the normal boiling point a formula of the type (8) becomes almost if not quite as accurate as the experimental data, but the best value for the constants A, B over this temperature range are not quite the same as the best values for the whole range from triple point to critical point. For argon an excellent fit of the experimental vapour pressures between the triple point and the normal boiling point and of the calorimetrically determined enthalpy of evaporation is attained with the values

$$A=5.13 \qquad B=5.21 \qquad \text{(temperatures below n.b.p.)} \tag{3.48.10}$$

$$\Delta_e H=5.21RT_c. \tag{3.48.11}$$

In the eighth row of table 3.8 are given the temperatures T_s at which the vapour pressure has a value one fiftieth of the critical pressure. In the ninth row are given values of the ratio T_s/T_c. These are all close to 0.58.

In the tenth row of this table are given values of the proper enthalpy of evaporation in the low temperature range where it is nearly independent of the temperature. In the eleventh row are given values of $\Delta_e H/RT_s$. All these values lie near to 9.0. Since $\Delta_e H/T_s$ is the entropy of evaporation, this aspect of the principle of corresponding states may be formulated thus: the entropy of evaporation at corresponding temperatures, e.g. temperatures at which the vapour pressure is one fiftieth the critical pressure, has a common value. The older *rule of Trouton* that substances should have the same entropy of evaporation at their normal boiling points is not in accord with the principle of corresponding states and is in somewhat less good agreement with the facts.

In the twelfth row of the table are given values of V_m the proper volume of the liquid at temperatures just above the triple point and in the thirteenth row values of the ratio V_m/V_c. These values are all near to 0.375.

§3.49 *Corresponding states of solids*

The principle of corresponding states has a much more restricted applicability to solids. It however applies with high accuracy to the group of the inert elements Ne, Ar, Kr, Xe. The relevant data for comparison are given in table 3.9. In the first three rows are given values of T_c, V_c, and P_c.

In the fourth row are given values of the triple point temperature T_t and in the fifth row values of the ratio T_t/T_c. All these values are near to 0.555.

In the sixth row are given values of the proper enthalpy of fusion $\Delta_f H$ divided by R and in the seventh row values of the entropy of fusion $\Delta_f S$ divided by R. These are all near to 1.69.

In the eighth row are given values of P_t, the triple point pressure, and in the ninth row values of the ratio $100P_t/P_c$. These are all near to 1.4.

Finally in the tenth and eleventh rows are given the proper volumes V^L and V^S of the liquid and solid respectively both at the triple point. In the twelfth row are given the ratios V^L/V^S, all near to 1.15.

TABLE 3.9

Corresponding states of solids

	Formula	Ne	Ar	Kr	Xe
1	T_c/K	44.8	150.7	209.4	289.8
2	$V_c/\text{cm}^3\ \text{mole}^{-1}$	41.7	75.3	92.1	118.8
3	P_c/atm	26.9	48.0	54.1	58.0
4	T_t/K	24.6	83.8	116.0	161.3
5	T_t/T_c	0.549	0.557	0.553	0.557
6	$\Delta_f H/R\ \text{K}$	40.3	141.3	196.2	276
7	$\Delta_f H/RT_t$	1.64	1.69	1.69	1.71
8	P_t/atm	0.425	0.682	0.721	0.810
9	$100P_t/P_c$	1.58	1.42	1.33	1.40
10	$V^L/\text{cm}^3\ \text{mole}^{-1}$		28.14	34.13	42.68
11	$V^S/\text{cm}^3\ \text{mole}^{-1}$		24.61	29.65	37.09
12	V^L/V^S		1.144	1.151	1.151

§3.50 *Two simple equations of state*

Many attempts have been made in the past to represent the equation of state of gas and liquid throughout the whole P–V–T domain by an analytical formula. It is now known that it is not possible so to represent the experimental data accurately except by complicated and unwieldy formulae of little interest. On the other hand the distinction between liquid and gas and the existence of a critical point can be deduced qualitatively from various quite simple equations of state. Of these we shall mention only two of the simplest.

The earliest attempt to describe semi-quantitatively the behaviour of a real fluid was made by van der Waals. His well-known formula is

$$(P+a/V_m^2)(V_m-b)=RT \qquad 3.50.1$$

but in the present context it is more convenient to write it as

$$PV_m=RT(1-4y)^{-1}-a/V_m \qquad 3.50.2$$

where

$$y=b/4V_m. \qquad 3.50.3$$

Van der Waals assumed a model of spherical molecules of volume $b/4L$ or yV_m/L. He also assumed that the proper attractive potential energy could be expressed as $-a/V_m$.

From (1) or (2) we derive for the proper total energy U_m

$$U_m = -a/V_m \qquad 3.50.4$$

and for the proper entropy S_m

$$-S_m/R = \ln\{y/(1-4y)\}. \qquad 3.50.5$$

In (4) the zero of energy is that at zero density. In (5) the arbitrary constant in the entropy is chosen so that in the limit of low density $S_m/R \to -\ln y$.

It is now known that formula (5) for the entropy is valid only for densities so low that y^2 is negligible; in other words it leads to a correct contribution to the second virial coefficient, but very inaccurate contributions to all higher virial coefficients. Formula (4) for the energy by contrast is inaccurate at low densities but is a useful approximation at high densities.

We shall compare and contrast equation (2) with the equally simple formula*

$$PV_m = RT(1-y)^{-4} - a/V_m \qquad 3.50.6$$

from which follows

$$U_m = -a/V_m \qquad 3.50.7$$

$$-S_m/R = \ln\{y/(1-y)\} + 3y(1-\tfrac{1}{2}y)/(1-y)^2 + y^3/3(1-y)^3. \qquad 3.50.8$$

In the limit of high temperatures the term $-a/V_m$ in (6) becomes unimportant compared with the term proportional to T. It is known that the latter term is correct up to y^3 in contrast to the van der Waals term $RT(1-4y)$ which is correct only up to y. In the limit of high temperatures we have the virial expansions according to van der Waals

$$PV_m/RT = 1 + 4y + 16y^2 + 64y^3 + 256y^4 + 1024y^5 + \ldots \qquad 3.50.9$$

and according to (6)

$$PV_m/RT = 1 + 4y + 10y^2 + 20y^3 + 35y^4 + 56y^5 + \ldots \qquad 3.50.10$$

whereas the accurate expansion for non-attracting rigid spheres is known to be

$$PV_m/RT = 1 + 4y + 10y^2 + 18.36y^3 + 29.4y^4 + \ldots. \qquad 3.50.11$$

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* Guggenheim, Molec. Phys. 1965 **9** 199; Longuet-Higgins and Widom, Molec. Phys. 1964 **8** 549.

We shall now compare other consequences of formulae (2), (4), (5) on the one hand and (6), (7), (8) on the other. Where possible we shall also compare with experimental data on argon. The complete comparison is given in table 3.10. We first derive formulae relating to the critical point. These are determined by the simultaneous conditions

$$\partial P/\partial y=0 \qquad \partial^2 P/\partial y^2=0 \tag{3.50.12}$$

which lead to the values of y_c and of V_c/b and of a/RT_cV_c given in the first three rows.

TABLE 3.10

Comparison of equations of state

		Van der Waals	Modified equation	Experiment
1	y_c	0.083	0.126	
2	V_c/b	3	1.98	
3	a/RT_cV_c	1.125	1.37	
4	$T_B/T_c=a/RT_cb$	3.38	2.72	2.73
5	$(PV/RT)_c$	0.375	0.33	0.29
6	$a/RT_tV^L_m$	(8.56)	(8.56)	8.56
7	y^L	0.221	0.416	
8	V^L_m/b	1.13	0.600	
9	V^L_m/V_c	0.377	0.303	0.374
10	$\ln(PV^L_m/RT)$	−7.40	−6.01	−5.89
11	P_cV^L/RT_c	0.141	0.109	0.108

We next obtain the Boyle temperature T_B given by

$$RT_B=a/b \tag{3.50.13}$$

and the values of the ratio T_B/T_c are given in the fourth row.

The fifth row gives values of $(PV/RT)_c$ obtained from the values in the first and third rows by means of the equation

$$(PV/RT)_c=1-4y_c-a/RT_cV_c \tag{3.50.14}$$

or the equation

$$(PV/RT)_c=(1-y_c)^4-a/RT_cV_c. \tag{3.50.15}$$

Hitherto we have not assumed any experimental values. To obtain quantitative results concerning the liquid denoted by the superscript ^{L} at or near the triple point denoted by the subscript $_t$ we equate $a/RT_tV^L_m$ to the experimental value for argon, or indeed any substance conforming to corresponding states with respect to argon, of Δ_eU/RT_t where Δ_eU is the energy of evaporation. This is shown in the sixth row. We now put $PV^L_m=0$ in (2) and in (6) to obtain the values of y^{L} in the seventh row and thence the values of $V_{\mathrm{m}}^{\mathrm{L}}/b$ in the eighth row. By combining the figures in the second and eighth rows we obtain the values of $V_{\mathrm{m}}^{\mathrm{L}}/V_{\mathrm{c}}$ in the ninth row.

For the equilibrium between liquid and vapour at the triple point we have

$$\mu^{\mathrm{G}}=\mu^{\mathrm{L}}. \qquad 3.50.16$$

If we treat the vapour as a perfect gas and set $PV_{\mathrm{m}}^{\mathrm{L}}/RT=0$ we have the equations

$$\ln y^{\mathrm{G}}-1=a/RT_{\mathrm{t}}V_{\mathrm{m}}^{\mathrm{L}}+\ln\{y^{\mathrm{L}}/(1-4y^{\mathrm{L}})\} \qquad 3.50.17$$

or alternatively

$$\ln y^{\mathrm{G}}-1=a/RT_{\mathrm{t}}V_{\mathrm{m}}^{\mathrm{L}}+\ln\{y^{\mathrm{L}}/(1-y^{\mathrm{L}})\}+3y^{\mathrm{L}}(1-\tfrac{1}{2}y^{\mathrm{L}})/(1-y^{\mathrm{L}})^2 + y^{\mathrm{L}3}/3(1-y^{\mathrm{L}})^3. \qquad 3.50.18$$

Using

$$y^{\mathrm{G}}/y^{\mathrm{L}}=V_{\mathrm{m}}^{\mathrm{L}}/V_{\mathrm{m}}^{\mathrm{G}}=PV_{\mathrm{m}}^{\mathrm{L}}/RT \qquad 3.50.19$$

we can rewrite (17) as

$$\ln(PV_{\mathrm{m}}^{\mathrm{L}}/RT_{\mathrm{t}})=1+a/RT_{\mathrm{t}}V_{\mathrm{m}}^{\mathrm{L}}-\ln(1-4y^{\mathrm{L}}) \qquad 3.50.20$$

and (18) as

$$\ln(PV_{\mathrm{m}}^{\mathrm{L}}/RT_{\mathrm{t}})=1+a/RT_{\mathrm{t}}V_{\mathrm{m}}^{\mathrm{L}}-\ln(1-y^{\mathrm{L}})+3y^{\mathrm{L}3}(1-\tfrac{1}{2}y^{\mathrm{L}})/(1-y^{\mathrm{L}})^2 + y^{\mathrm{L}3}/3(1-y^{\mathrm{L}})^3. \qquad 3.50.21$$

Using the values of $a/RT_{\mathrm{t}}V_{\mathrm{m}}^{\mathrm{L}}$ in the sixth row and of y^{L} in the seventh row we obtain the values of $\ln(PV_{\mathrm{m}}^{\mathrm{L}}/RT_{\mathrm{t}})$ in the tenth row.

We observe that the equation of state (6) in contrast to the van der Waals equation (2) leads to remarkably good agreement with experiment except for expressions containing V_{c}. This is not surprising. Because $\partial V/\partial P \to \infty$ at the critical point a small inexactitude in the P–V curve may affect P_{c} only slightly but will have a pronounced effect on V_{c}. This is borne out by multiplying $(PV/RT)_{\mathrm{c}}$ by $V_{\mathrm{t}}/V_{\mathrm{c}}$ and obtaining the values of $P_{\mathrm{c}}V_{\mathrm{t}}/RT_{\mathrm{c}}$ in the last line of the table.

§3.51 *Zero-temperature entropy in crystals*

In §3.26 we gave formula (3.26.4) for the conventional entropy of a slightly imperfect gaseous element composed of monatomic molecules. This formula is composed additively of contributions from

(a) translational degrees of freedom
(b) electronic degrees of freedom
(c) gas imperfection.

In §3.28 we gave, for the conventional entropy of a slightly imperfect gas composed of linear molecules, in formulae (3.28.5) and (3.28.10) respectively, the further contributions from rotational and vibrational degrees of freedom.

In §3.29 we gave formula (3.29.4) for the rotational contribution to the entropy of a slightly imperfect gas composed of non-linear molecules and formula (3.29.7) for the vibrational degrees of freedom.

Thus all the conventional formulae for a slightly imperfect gas include contributions from

(a) translational degrees of freedom
(b) electronic degrees of freedom, if any
(c) gas imperfection
(d) rotational degrees of freedom, if any
(e) vibrational degrees of freedom, if any

All other possible contributions are excluded, in particular

(f) intranuclear degrees of freedom
(g) mixing of isotopes.

There are two good reasons for disregarding the contribution of intranuclear degrees of freedom. In the first place they are in many cases not known. In the second place under terrestrial conditions the nuclear contribution of each nuclidic species is a constant independent of temperature, pressure, phase, composition, and chemical change.

The contribution due to isotopic mixing is ignored because it remains constant as long as the isotopic composition remains unchanged. Variations in isotopic composition will be discussed in §3.55.

We have now reinterpreted what we mean by the conventional proper entropy $S^{\mathrm{G}}_{\mathrm{m}}(T, P)$ of a slightly imperfect single gas at a chosen temperature and pressure. Since any entropy change can be determined by calorimetric and related measurements, we can in particular determine

$$S^{\mathrm{G}}_{\mathrm{m}}(T, P) - S^{\mathrm{S}}_{\mathrm{m}}(T', P') \qquad 3.51.1$$

where the superscript $^{\mathrm{S}}$ denotes the solid crystalline phase. If T' is sufficiently small we can use Debye's approximation (3.32.2) to extrapolate $T' \to 0$ so as to obtain a value of $S^{\mathrm{S}}_{\mathrm{m}}(0, P')$. The dependence of $S^{\mathrm{S}}_{\mathrm{m}}$ on P is negligible, and in fact vanishes as $T \to 0$, and we therefore abbreviate $S^{\mathrm{S}}_{\mathrm{m}}(0, P)$ to $S^{\mathrm{S}}_{\mathrm{m}}(0)$. We thus have a calorimetric value of

$$S^{\mathrm{G}}_{\mathrm{m}}(T, P) - S^{\mathrm{S}}_{\mathrm{m}}(0). \qquad 3.51.2$$

The quantity specified in (2) is often called the *calorimetric entropy* of the gas at the given temperature and pressure, whereas the conventional entropy of a gas $S^{\mathrm{G}}_{\mathrm{m}}(T, P)$ is often called the *spectroscopic entropy* of the gas at the given temperature and pressure.

It is found experimentally that for all elements the calorimetric entropy is equal to the spectroscopic entropy. (The exceptional behaviour of hydrogen will be discussed in §3.56.) Thus

$$S^{\mathrm{G}}_{\mathrm{m}}(T, P) - S^{\mathrm{S}}_{\mathrm{m}}(0) = S^{\mathrm{G}}_{\mathrm{m}}(T, P) \qquad \text{(element)} \qquad 3.51.3$$

and consequently

$$S^{\mathrm{S}}_{\mathrm{m}}(0) = 0 \qquad \text{(element).} \qquad 3.51.4$$

Formula (4) expresses our earlier definition of conventional entropy given in §3.25. We have now verified that the convention used in §3.25 is equivalent to the convention described in the present section.

It is found experimentally that the equations (3) and (4) also hold for most compounds, but there are about half a dozen well-established exceptions.

§3.52 *Two numerical examples*

We shall now illustrate the content of §3.51 by two numerical examples. We choose N_2 and CO.

To calculate the conventional or spectroscopic entropy of nitrogen we use the following data. The proper mass is 28.02 g mole^{-1}. The rotational characteristic temperature Θ_{r} is 2.87 K and the vibrational characteristic temperature Θ_{v} is 3.35×10^3 K. The symmetry number s is 2. At the boiling point 77.32 K and a pressure of 1 atm we have, using (3.27.4) and (3.28.5)

$$\begin{aligned} S^{\mathrm{G}}_{\mathrm{m}}(T_{\mathrm{b}})/R &= \tfrac{7}{2} + \tfrac{5}{2}\ln(T_{\mathrm{b}}/4.333\ \mathrm{K}) + \tfrac{3}{2}\ln(M/\mathrm{g\ mole}^{-1}) + \ln(T_{\mathrm{b}}/s\Theta_{\mathrm{r}}) \\ &= \tfrac{7}{2} + \tfrac{5}{2}\ln(77.32/4.333) + \tfrac{3}{2}\ln 28.02 + \ln\{77.32/(2\times 2.87)\} \\ &= 3.50 + 7.20 + 5.00 + 2.60 = 18.30. \end{aligned} \qquad 3.52.1$$

The contributions from the vibrational degree of freedom and from gas imperfection are negligible.

We next calculate the calorimetric entropy. As usual we use superscripts $^{\mathrm{S}}$ for solid, $^{\mathrm{L}}$ for liquid, and $^{\mathrm{G}}$ for gas. We use subscripts $_{\mathrm{tr}}$ to denote a transition, $_{\mathrm{f}}$ to denote fusion, and $_{\mathrm{e}}$ to denote evaporation. We use the following data

$$\int_0^{T_{\mathrm{tr}}} C^{\mathrm{S}} \mathrm{d} \ln T = 6.49\ \mathrm{cal\ K^{-1}\ mole^{-1}}$$

including an extrapolation from 15 K to 0 K,

$$\int_{T_{\mathrm{tr}}}^{T_{\mathrm{f}}} C^{\mathrm{S}} \mathrm{d} \ln T = 5.59 \text{ cal K}^{-1} \text{ mole}^{-1}$$

$$\int_{T_{\mathrm{f}}}^{T_{\mathrm{b}}} C^{\mathrm{L}} \mathrm{d} \ln T = 2.73 \text{ cal K}^{-1} \text{ mole}^{-1}$$

$$\begin{aligned} T_{\mathrm{tr}} &= 35.61 \text{ K} \qquad & \Delta_{\mathrm{tr}} H &= 54.71 \text{ cal mole}^{-1} \\ T_{\mathrm{f}} &= 63.14 \text{ K} & \Delta_{\mathrm{f}} H &= 172.3 \text{ cal mole}^{-1} \\ T_{\mathrm{b}} &= 77.32 \text{ K} & \Delta_{\mathrm{e}} H &= 1332.9 \text{ cal mole}^{-1}. \end{aligned}$$

Hence the calorimetric entropy at the boiling point and at one atmosphere

$$\begin{aligned} &S_{\mathrm{m}}^{\mathrm{G}}(T_{\mathrm{b}}) - S_{\mathrm{m}}^{\mathrm{S}}(0) \\ &= (6.49 + 54.71/35.61 + 5.59 + 172.3/63.14 + 2.73 + 1332.9/77.32) \text{ cal K}^{-1} \text{ mole}^{-1} \\ &= (6.49 + 1.54 + 5.59 + 2.73 + 2.73 + 17.24) \text{ cal K}^{-1} \text{ mole}^{-1} \\ &= 36.32 \text{ cal K}^{-1} \text{ mole}^{-1} \end{aligned}$$

and consequently

$$\{S_{\mathrm{m}}^{\mathrm{G}}(T_{\mathrm{b}}) - S_{\mathrm{m}}^{\mathrm{S}}(0)\}/R = 18.3. \qquad 3.52.2$$

From (1) and (2) we conclude that the conventional entropy $S_{\mathrm{m}}^{\mathrm{S}}(0)$ of the solid at 0 K is zero.

When we do precisely analogous calculations for carbon monoxide we obtain at 1 atm

$$\begin{aligned} S_{\mathrm{m}}^{\mathrm{G}}(T_{\mathrm{b}})/R &= \tfrac{7}{2} + \tfrac{5}{2} \ln(81.61/4.333) + \tfrac{3}{2} \ln 28.01 + \ln(81.61/2.77) \\ &= 3.50 + 7.34 + 5.00 + 3.38 = 19.22 \qquad 3.52.3 \end{aligned}$$

$$\begin{aligned} &S_{\mathrm{m}}^{\mathrm{G}}(T_{\mathrm{b}}) - S_{\mathrm{m}}^{\mathrm{S}}(0) \\ &= (10.09 + 151.3/61.55 + 1.23 + 199.7/68.09 \\ &\qquad + 2.61 + 1443.6/81.61) \text{ cal K}^{-1} \text{ mole}^{-1} \\ &= (10.09 + 2.46 + 1.23 + 2.93 + 2.61 + 17.69) \text{ cal K}^{-1} \text{ mole}^{-1} \\ &= 37.01 \text{ cal K}^{-1} \text{ mole}^{-1} \end{aligned}$$

and consequently

$$\{S_{\mathrm{m}}^{\mathrm{G}}(T_{\mathrm{b}}) - S_{\mathrm{m}}^{\mathrm{S}}(0)\}/R = 18.6. \qquad 3.52.4$$

Comparing (3) and (4) we find for the conventional entropy of the crystal at 0 K

$$S_{\mathrm{m}}^{\mathrm{S}}(0)/R = 0.6 = \ln 2 \qquad 3.52.5$$

within the experimental accuracy.

§3.53 *Statistical-mechanical interpretation*

We recall that by definition the vanishing of the conventional entropy of a crystal extrapolated to $T \to 0$

$$S^{\mathrm{s}}_{\mathrm{m}}(0)=0 \qquad 3.53.1$$

holds for all elements. The special behaviour of hydrogen is discussed in §3.56. Formula (1) also holds for the vast majority of compounds. The best established exceptions are CO, NNO, NO, H_2O.

Classical thermodynamics has nothing to add to this statement. It is however instructive and interesting to discuss the statistical-mechanical interpretation. The interpretation of (1) is that the lowest energy level of the crystal is non-degenerate. This implies that the structure of the crystal is perfectly regular showing no kind of randomness.

The condition (1) found for most crystals states that the conventional zero-temperature entropy of the crystal is zero. This means that the contributions to the entropy from the translational, electronic, rotational, and internal vibrational degrees of freedom are all zero. In other words disregarding intranuclear degrees of freedom and isotopic composition, we may say that no other degrees of freedom contribute anything to the entropy. Statistical theory tells us that this corresponds to the crystal being in a perfectly ordered state, provided we disregard intranuclear degrees of freedom and isotopic composition. Thus a combination of statistical theory with experimental data tells us that as the temperature decreases, most crystals tend towards a state of perfect order apart from intranuclear phenomena and isotopic composition. More strictly we should say that this is how the crystal appears to behave judged by the experimental data in the region of 0 K.

§3.54 *Simple typical exceptions*

We shall now consider exceptions to the general rule $S^{\mathrm{s}}_{\mathrm{m}}(0) = 0$. For this purpose it is convenient to define a number o by

$$S^{\mathrm{s}}_{\mathrm{m}}(0)=R \ln o \qquad 3.54.1$$

so that usually $o=1$. The two simplest exceptions are CO and NNO. In both cases within the experimental accuracy $o=2$. The statistical interpretation of the value 2 for o is that instead of perfect order in the crystal, there are two possible orientations for each molecule and the molecules are randomly distributed between these two orientations. This is what we should expect to happen in the case of a linear molecule whose field of force is nearly but not quite symmetrical so that the molecule can be reversed end for end without an appreciable energy change. Statistical theory tells us that the equilibrium distribution of directions will remain random down to temperatures at which kT is comparable with the energy difference in the two orientations. At temperatures where kT is much smaller than the energy difference between the two orientations, then only one orientation will be stable, but at such low temperatures it may well be that the molecules have not sufficient energy to turn round. In simple words when the crystal is so cold that the molecules have a preference for one orientation they have too little energy (are 'too cold') to change their orientations. Such a crystal at the lowest temperatures will remain in a state with $o=2$ and this state is metastable with respect to the ideal unrealizable state of ordered orientation with $o=1$. It is believed that this is a true description of the behaviour of crystalline CO and NNO at the lowest temperatures. It is interesting to note that the SCO molecule is not sufficiently symmetrical to behave in this way and the experimental data are consistent with $o=1$.

The case of NO is somewhat more complicated. It is suggested that at the lowest temperatures the molecular unit is $\begin{smallmatrix}\mathrm{NO}\\ \mathrm{ON}\end{smallmatrix}$ and that owing to the similarity between N and O atoms the two orientations $\begin{smallmatrix}\mathrm{NO}\\ \mathrm{ON}\end{smallmatrix}$ and $\begin{smallmatrix}\mathrm{ON}\\ \mathrm{NO}\end{smallmatrix}$ have nearly equal energies. There would then be a random distribution over these two orientations. This would lead to a value of $o=2$ for the molecular unit N_2O_2; the corresponding value of o expressed in terms of the molecule NO is $2^{\frac{1}{2}}$ and this value is in agreement with experiment within the estimated accuracy.

The other well established case of $o>1$ believed due to simple orientational randomness is that of ice. To account for the experimental data the following assumptions are made.

(1) In ice each oxygen atom has two hydrogens attached to it at distances about 0.95 Å forming a molecule, the HOH angle being about 105° as in the gas molecule.

(2) Each HOH molecule is oriented so that its two H atoms are directed approximately towards two of the four O atoms which surround it tetrahedrally.

(3) The orientations of adjacent HOH molecules are such that only one H atom lies approximately along each O–O axis.

(4) Under ordinary conditions the interaction of non-adjacent molecules is not such as to stabilize appreciably any one of the many configurations satisfying the preceding conditions relative to the others.

On these assumptions Pauling* calculated that theoretically $o=\frac{3}{2}$. Experimentally this value is verified for both H_2O and D_2O.

* Pauling, J. Amer. Chem. Soc. 1935 **57** 2680.

§3.55 *Isotopic mixing*

The presence of isotopes can have three effects, which we shall now consider.

The first effect is that $\ln M$ must be replaced by the suitably weighted sum

$$\sum_i x_i \ln M_i \qquad 3.55.1$$

where x_i is the mole fraction of the particular isotope i having a proper mass M_i. Similarly $\ln \Theta_r$ must be replaced by

$$\sum_i x_i \ln \Theta_{ri} \qquad 3.55.2$$

where Θ_{ri} is the value of Θ_r for the particular isotope i. The terms in Θ_v must similarly be replaced by suitably weighted averages. It should not be necessary to give details, especially since in almost all cases it is sufficiently accurate to replace these averaging rules by the simpler rules of replacing

$$M \quad \text{by} \quad \sum_i x_i M_i \qquad 3.55.3$$

$$\Theta_r \quad \text{by} \quad \sum_i x_i \Theta_{ri} \qquad 3.55.4$$

$$\Theta_v \quad \text{by} \quad \sum_i x_i \Theta_{vi}. \qquad 3.55.5$$

It is only in the cases of H_2, D_2, and possibly other very light molecules containing H, D that these simpler averaging rules may not always be sufficiently accurate.

The term H^0 occurring in H_m and in μ, but not in S_m, must likewise be replaced by the weighted average

$$\sum_i x_i H_i^0. \qquad 3.55.6$$

The second effect is that any phase whether solid, liquid, or gaseous, consisting of a mixture of isotopic molecules in mole fractions x_i, has a proper entropy exceeding the proper entropy of similar phases of the pure isotopes at the same temperature and pressure, and this excess is

$$-R \sum_i x_i \ln x_i \qquad 3.55.7$$

which is always positive since $x_i < 1$. We shall meet formula (7) again in chapter 4. In the present context we need only note that as long as the solid and gas have the same isotopic composition, the terms of the form (7) cancel and so contribute nothing to *o*.

The third effect to be considered is that associated with difference in symmetry. Let us consider the particular example of Cl_2. There are three kinds of molecules $^{35}Cl^{35}Cl$, $^{37}Cl^{37}Cl$, and $^{35}Cl^{37}Cl$. For the molecules $^{35}Cl^{35}Cl$ and $^{37}Cl^{37}Cl$ the symmetry number s is 2, while for the molecule $^{35}Cl^{37}Cl$ it is 1. In the crystal, on the other hand, o for $^{35}Cl^{37}Cl$ will have the value 2 because each molecule can be reversed to give a physically distinct state of the crystal of effectively equal energy, whereas for $^{35}Cl^{35}Cl$ and $^{37}Cl^{37}Cl$ there are not two distinguishable orientations of effectively equal energy and so o is 1. Thus the product so has the same value 2 for all three types of molecules. Ignoring the isotopic composition means then assigning to $^{35}Cl^{37}Cl$ a fictitious value of $s=2$ instead of $s=1$ and to o a fictitious value $o=1$ instead of $o=2$. When we compare the entropies of the gas and the crystal, and it is only in such comparisons that the values assigned to S_{m} have any significance, the two errors cancel.

It is instructive to compare the behaviours of CO and N_2 with those of $^{35}Cl^{37}Cl$ and $^{35}Cl^{35}Cl$. We saw in §3.52 that for CO the value of o is 2 while of course $s=1$. We should however obtain correct results if we assumed as for N_2 that $o=1$ with $s=2$, using this effective symmetry number because CO is an effectively symmetrical molecule.

The same principle holds in more complicated cases. For example comparing the isotopic molecules CH_4, CH_3D, CH_2D_2 we see that for the first $s=12$, $o=1$, for the second $s=3$, $o=4$ and for the third $s=2$, $o=6$ so that in all three cases the product so is 12.

§3.56 *The exceptional case of hydrogen*

Hydrogen is exceptional in several respects. This is due partly to its molecule having such a small moment of inertia with a consequently high value of the rotational characteristic temperature $\Theta_{\mathrm{r}}=85.4$ K. It is also partly due to the molecules having an exceptionally small field of force so that even at very low temperatures they still rotate in the crystal. We shall not here go into the theory* of the behaviour of hydrogen as this would take us too far afield. We shall merely state the facts sufficiently to show how the various thermodynamic formulae must be used so as to obtain correct results.

For the sake of consistency we define the conventional zero of entropy precisely as for all other molecules, so the formulae of §3.26 to §3.28 are valid for the gas. As regards the physical meaning of this convention, instead of completely neglecting the intranuclear degrees of freedom we ignore the

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* Fowler and Guggenheim, Statistical Thermodynamics 1939, Cambridge University Press § 531.

contributions due to any intranuclear degrees of freedom other than resultant nuclear spin, and the contribution due to the spin of the two nuclei in a hydrogen molecule is taken to be the same as if the nuclei were present in independent atoms. Any actual deviation from this will then appear in o.

We shall first consider the gas. The usual formulae for gases with diatomic molecules are applicable only at temperatures large compared with Θ_r and consequently for H_2 they are valid only above about 300 K.

At ordinary temperatures and a fortiori at lower temperatures the vibrational degree of freedom in H_2 may be ignored. As the temperature decreases from about 300 K to about 45 K the rotational contributions to the thermodynamic functions drop from the values for a pair of classical degrees of freedom to values for unexcited degrees of freedom. In particular at temperatures around 45 K or lower

$$-\mu_{\mathrm{rot}}/RT = S_{\mathrm{rot}}/R = \tfrac{3}{4}\ln 3 \qquad 3.56.1$$

$$H_{\mathrm{rot}}/RT = 0. \qquad 3.56.2$$

The constant term $\frac{3}{4}\ln 3$ in (1) is due to the fact that hydrogen behaves as a mixture of $\frac{1}{4}$ para hydrogen with a proper rotational entropy zero at low temperatures and $\frac{3}{4}$ ortho hydrogen with a proper rotational entropy $R\ln 3$ at low temperatures.

Turning now to the crystal, let us first ignore any experimental data below 12 K and extrapolate smoothly the data between 20 K and 12 K in the usual way. We thus obtain well determined values of

$$S_{\mathrm{m}}^{\mathrm{G}}(T) - S_{\mathrm{m}}^{\mathrm{S}}(0) = S_{\mathrm{m}}^{\mathrm{G}}(T) - R\ln o. \qquad 3.56.3$$

We may use the usual formula for $S_{\mathrm{m}}^{\mathrm{G}}(T)$ with $T > 300$ K or alternatively formula (1) for $S_{\mathrm{m}}^{\mathrm{G}}(T)$ with $T < 45$ K; by either procedure we obtain a value for o agreeing within the experimental error with

$$\ln o = \tfrac{3}{4}\ln 3. \qquad 3.56.4$$

We notice that the conventional zero-temperature entropy of the crystal obtained by smooth extrapolation from 12 K is the same as the rotational entropy in the gas below 45 K.

This would complete the picture of ordinary hydrogen were it not for the existence of experimental data on the crystal between 12 K and 2 K. In this range the entropy decreases with anomalous rapidity. In fact the heat capacity not only is anomalously greater than corresponds to the form aT^3, but it actually increases as the temperature decreases below 6 K. On theoretical grounds it is clear that the ortho molecules are somehow beginning to 'line up' with a consequent decrease of entropy. There can be little doubt that if these experimental data extended to still lower temperatures the heat capacity would eventually become normal again after there had been a total loss of proper entropy $\frac{3}{4}R \ln 3$. If we then determined $S_{\mathrm{m}}^{\mathrm{S}}(0)$ from here instead of by extrapolation from 12 K, we should find

$$o=1. \tag{3.56.5}$$

Up to this point we have assumed that the crystal, like the gas, consists of the ordinary metastable mixture of $\frac{1}{4}$ para hydrogen and $\frac{3}{4}$ ortho hydrogen. For a mixture of this composition the contributions of nuclear spin to the entropy are normal and so their conventional omission leads to no complications. If however the crystalline hydrogen were converted to stable pure para hydrogen there would be a decrease in the contributions to the proper entropy of $\frac{3}{4}R \ln 3$ from the nuclear spins and of $-R(\frac{3}{4} \ln \frac{3}{4} + \frac{1}{4} \ln \frac{1}{4})$ from the mixing of the para and ortho molecules. This would manifest itself as

$$o=\tfrac{1}{4}. \tag{3.56.6}$$

The conventional zero-temperature entropy of stable para hydrogen has the negative value

$$S_{\mathrm{m}}^{\mathrm{S}}(0) = -R \ln 4 \qquad \text{(para hydrogen)}. \tag{3.56.7}$$

For deuterium D_2 the general picture is similar with several differences of detail. The gas behaves like other diatomic gases at temperatures exceeding 200 K. Between this temperature and about 25 K, the rotational contributions to the thermodynamic functions drop from their values for a pair of classical degrees of freedom to values for unexcited degrees of freedom. In particular below 25 K

$$-\mu_{\mathrm{rot}}/RT = S_{\mathrm{rot}}/R = \tfrac{1}{3} \ln 3 \tag{3.56.8}$$

$$H_{\mathrm{rot}}/RT = 0. \tag{3.56.9}$$

The constant term $\frac{1}{3} \ln 3$ in (8) is due to the fact that D_2 behaves as a mixture of $\frac{2}{3}$ ortho deuterium with a proper rotational entropy zero at low temperatures and $\frac{1}{3}$ para deuterium with a proper rotational entropy $R \ln 3$ at low temperatures.

For the crystal similarly, if one extrapolates in the usual way from a temperature between 20 K and 10 K one obtains

$$S_{\mathrm{m}}^{\mathrm{S}}(0)/R = \ln o = \tfrac{1}{3} \ln 3. \tag{3.56.10}$$

For the ordinary metastable mixture of $\frac{2}{3}$ ortho deuterium and $\frac{1}{3}$ para deuterium the contributions of nuclear spin to the entropy are normal and so their conventional omission leads to no complications. When, however, the crystalline deuterium is converted to stable pure ortho deuterium there is a decrease of $R(\frac{1}{3}\ln 3+\frac{2}{3}\ln 6)$ in the contribution of nuclear spins to the proper entropy and a decrease of $-R(\frac{1}{3}\ln\frac{1}{3}+\frac{2}{3}\ln\frac{2}{3})$ from the mixing of the ortho and para molecules. If we assume that at the lowest temperature the molecules line up, as we know to be the case with H_2, this will manifest itself as

$$o=\frac{6}{9}=\frac{2}{3}.$$

The conventional zero-temperature entropy of stable ortho deuterium is then

$$S^{\mathrm{S}}_{\mathrm{m}}(0)=R\ln\frac{2}{3}$$

which is negative.

§3.57 *Third law of thermodynamics and the Nernst heat theorem*

We recall our formulation of the third law in §1.66 which we now repeat.

By the standard methods of statistical thermodynamics it is possible to derive for certain entropy changes general formulae which cannot be derived from the zeroth, first, or second laws of classical thermodynamics. In the present chapter we have had three distinct examples of this type.

In the first place we have quoted in §§3.26–3.29 results of completely general validity for the entropy of gases at sufficiently high temperatures.

In the second place we have quoted a result of completely general validity for the increase of entropy when isotopes, or for that matter any other very similar molecules, are mixed at constant temperature and pressure.

In the third place we have quoted a result concerning the conventional zero-temperature entropy of a crystal, namely that its conventional value is usually but not always zero.

This last result, in the form quoted, is not altogether satisfactory because it admits exceptions without indicating how or when these occur. It is therefore desirable to try to replace this statement by a more definite statement not admitting exceptions. The following statement fulfils these requirements.

If ΔS denotes the increase in entropy in any isothermal change which we represent symbolically by

$$\alpha\rightarrow\beta \tag{3.57.1}$$

and we extrapolate ΔS to $T=0$ smoothly in the usual way, then if the states α and β are both internally stable, or if any kind of internal metastability present is not affected by the change $\alpha\rightarrow\beta$, then

$$\lim_{T\rightarrow 0}\Delta S=0. \tag{3.57.2}$$

If on the other hand α is internally metastable, while β is stable, so that the change $\alpha \to \beta$ removes the metastability, then

$$\lim_{T \to 0} \Delta S < 0. \qquad 3.57.3$$

The case where α is stable and β metastable does not arise, since the change $\alpha \to \beta$ would then be impossible. The above statements constitute an amended form* of a theorem first stated by Nernst and usually known as the *Nernst heat theorem.*

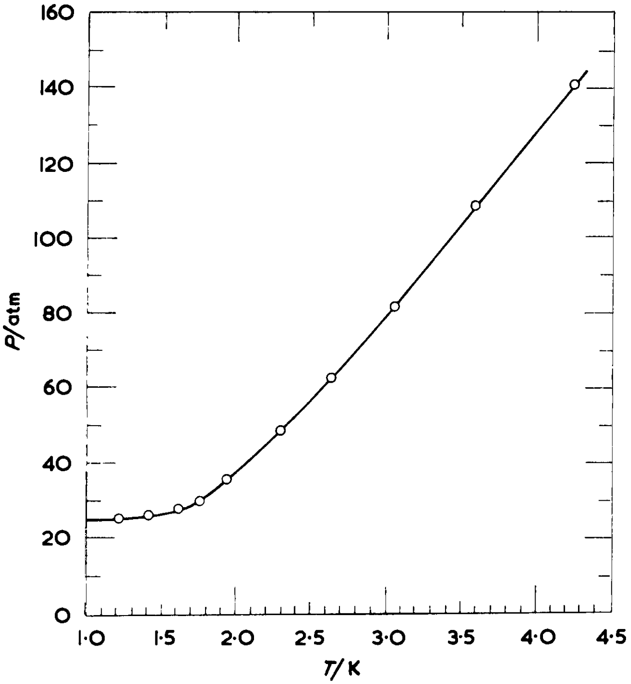

Fig. 3.13. Melting curve of helium

We shall now verify that the behaviour already described of crystals in the limit $T \to 0$ is in accord with the above general statement.

We observe that the several exceptional crystals for which o is not unity are in fact in internally metastable states with some form of randomness of arrangement of the molecules. If by any means it were possible to change such a crystal to the stable completely ordered modifications o would be reduced from a value greater than unity to the value unity and so (3) is satisfied.

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* Simon, Ergeb. Exakt. Naturw. 1930 **9** 222.

Examples of changes satisfying (2) are allotropic changes such as

white tin→grey tin
monoclinic sulphur→rhombic sulphur.

In each of these examples, although at low temperatures and ordinary pressures the first form is metastable with respect to the second, both forms are completely stable with respect to internal changes. In each case for both phases $o=1$ and so the equality (2) is obeyed.

Another interesting example is that of helium, the only substance which remains liquid down to $T=0$. The liquid is changed to solid under pressure. The relation between the pressure and the freezing temperature is shown in figure 3.13 from which it is clear that

$$\lim_{T\to 0} \mathrm{d}P/\mathrm{d}T=0. \qquad 3.57.4$$

But according to the Clapeyron relation this is equivalent to

$$\lim_{T\to 0} \Delta S/\Delta V=0. \qquad 3.57.5$$

But ΔV is certainly finite and so (5) implies

$$\lim_{T\to 0} \Delta S=0. \qquad 3.57.6$$

The most numerous and important examples of the relation (2) are those of chemical reactions between solid phases, for example

$$\mathrm{Ag}+\mathrm{I}\to\mathrm{AgI}.$$

These will be discussed in §6.11.

§3.58 *Thermal expansion at low temperatures*

It is an experimental fact that the coefficient of thermal expansion of solids and of liquid helium tends towards zero as the temperature is decreased. But according to Maxwell's relation (1.47.4), this implies that

$$\lim_{T\to 0} (\partial S/\partial P)_T=0. \qquad 3.58.1$$

If we integrate this from P_1 to P_2, we obtain

$$\lim_{T\to 0} \{S(T, P_2)-S(T, P_1)\}=0 \qquad 3.58.2$$

which is in accordance with the general relation (3.57.2).

This is the only example of the application of (3.57.2) to a simple physical change which we can discuss at this stage. In chapter 11 we shall consider an interesting application to variation of the strength of an applied magnetic field.

§3.59 *Unattainability of zero temperature*

The general laws formulated in the preceding sections concerning the behaviour of matter extrapolated to $T=0$ are equivalent to the following theorem*.

It is impossible by any procedure, no matter how idealized, to reduce the temperature of any system to zero temperature in a finite number of finite operations.

We shall now prove this equivalence. Let us consider a process (e.g. change of volume, change of external field, allotropic change) denoted formally by

$$\alpha \rightarrow \beta. \qquad 3.59.1$$

We shall use the superscripts $^\alpha$ and $^\beta$ to denote properties of the system in the states α and β respectively. Then the proper entropies of the system in these two states depend on the temperature according to the formulae

$$S^\alpha_{\mathrm{m}} = S^{0\alpha}_{\mathrm{m}} + \int_0^T (C^\alpha/T)\mathrm{d}T \qquad 3.59.2$$

$$S^\beta_{\mathrm{m}} = S^{0\beta}_{\mathrm{m}} + \int_0^T (C^\beta/T)\mathrm{d}T \qquad 3.59.3$$

where $S^{0\alpha}_{\mathrm{m}}$, $S^{0\beta}_{\mathrm{m}}$ are the limiting values of S^α_{m}, S^β_{m} for $T \rightarrow 0$. It is known from quantum theory that both the integrals converge. Suppose now that we start with the system in the state α at the temperature T' and that we can make the process $\alpha \rightarrow \beta$ take place adiabatically. Let the final temperature after the system has reached the state β be T''. We shall now consider the possibility or impossibility of T'' being zero. From the second law of thermodynamics we know that for an adiabatic process defined by its initial and final states the entropy increases if there is any irreversible change and remains constant if the change is completely reversible. It is therefore clear that the chances of attaining as low a final T as possible are most favourable when the change is completely reversible. We need therefore consider only such changes.

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* Simon, Science Museum Handbook 1937 **3** p. 61. All earlier discussions are unnecessarily restricted. Cf. Fowler and Guggenheim, Statistical Thermodynamics, Cambridge University Press 1939 § 538.

For a reversible adiabatic change (1) we have then by (2) and (3)

$$S_m^{0\alpha}+\int_0^{T'}(C^\alpha/T)\mathrm{d}T=S_m^{0\beta}+\int_0^{T''}(C^\beta/T)\mathrm{d}T. \qquad 3.59.4$$

If T'' is to be zero, we must then have

$$S_m^{0\beta}-S_m^{0\alpha}=\int_0^{T'}(C^\alpha/T)\mathrm{d}T. \qquad 3.59.5$$

Now if $S_m^{0\beta}-S_m^{0\alpha}>0$ it will always be possible to choose an initial T' satisfying (5) and by making the process α→β take place from this initial T' it will be possible to reach $T''=0$. From the premise of the unattainability of $T=0$ we can therefore conclude that

$$S_m^{0\beta}\leqq S_m^{0\alpha}. \qquad 3.59.6$$

Similarly we can show that if we can make the reverse process take place reversibly and adiabatically then we could reach $T''=0$ from an initial temperature T' satisfying

$$S_m^{0\alpha}-S_m^{0\beta}=\int_0^{T'}(C^\beta/T)\mathrm{d}T. \qquad 3.59.7$$

Further if $S_m^{0\alpha}-S_m^{0\beta}>0$, we can always choose an initial T' satisfying (7). From the unattainability of $T=0$ we can therefore conclude that

$$S_m^{0\alpha}\leqq S_m^{0\beta}. \qquad 3.59.8$$

From (6) and (8) we deduce

$$S_m^{0\alpha}=S_m^{0\beta} \qquad 3.59.9$$

which is precisely formula (3.57.2) of Nernst's heat theorem.

We can also show conversely that given (9), neither the process α→β nor the reverse process β→α can be used to reach $T=0$. For, assuming (9) to be true, we now have for the adiabatic process the initial temperature T' and the final temperature T'' related by

$$\int_0^{T'}(C^\alpha/T)\mathrm{d}T=\int_0^{T''}(C^\beta/T)\mathrm{d}T. \qquad 3.59.10$$

To reach $T''=0$ we should require

$$\int_0^{T'}(C^\alpha/T)\mathrm{d}T=0. \qquad 3.59.11$$

But, since $C^\alpha>0$ always, for any non-zero T' it is impossible to satisfy (11).

Hence the process cannot be used to reach $T=0$. The proof for the reverse process $\beta\rightarrow\alpha$ is exactly similar.

In the above argument we have assumed that the states α and β are connected by reversible paths. If all the phases concerned are phases in complete internal equilibrium the changes concerned must presumably be regarded as reversible. If any phase occurs naturally in metastable internal equilibrium, a process affecting it may or may not disturb the frozen metastability. If it does not disturb it, then the change may still be regarded as reversible, but otherwise it will be a natural irreversible change. We shall now verify that by using internally metastable phases we are still unable to reach $T=0$. In fact as foreshadowed above the irreversibility involved makes the task more difficult.

Suppose for example that α is internally metastable, while β is internally stable. Then according to the Nernst heat theorem

$$S_{\mathrm{m}}^{0\alpha} > S_{\mathrm{m}}^{0\beta}. \qquad 3.59.12$$

But the change $\alpha\rightarrow\beta$ is a natural irreversible process and the opposite change is impossible; hence the adiabatic change $\alpha\rightarrow\beta$ takes place with increase of entropy, so that

$$S_{\mathrm{m}}^{0\alpha} + \int_0^{T'} (C^{\alpha}/T)\mathrm{d}T < S_{\mathrm{m}}^{0\beta} + \int_0^{T''} (C^{\beta}/T)\mathrm{d}T. \qquad 3.59.13$$

Thus to attain $T''=0$ we must have

$$\int_0^{T'} (C^{\alpha}/T)\mathrm{d}T < S_{\mathrm{m}}^{0\beta} - S_{\mathrm{m}}^{0\alpha} < 0 \qquad 3.59.14$$

using (12). But since $C^{\alpha} > 0$ always, it is impossible to satisfy (14) and so we again find it impossible to reach $T=0$.

We shall revert to the subject of the unattainability of $T=0$ at the end of chapter 11 on magnetic systems.

§3.60 *Interfacial layers*

We complete this chapter by a consideration of interfacial layers. In a one-component system we cannot usually have more than one liquid phase and so we need consider only the interface between a liquid and its vapour. The interfacial tension of such an interface is called the *surface tension of the liquid.*

As we have seen, a one-component system with two bulk phases has one degree of freedom. We may accordingly treat the temperature as the independent variable; the pressure is then determined by the temperature. Thus the properties of the interfacial layer, in particular the surface tension, will be completely determined by the temperature. Our main task is therefore to consider how the surface tension depends on the temperature.

§3.61 *Temperature dependence of surface tension*

We begin with formula (1.57.3) which for a single component reduces to

$$-\mathrm{d}\gamma = S_A^\sigma \mathrm{d}T - \tau \mathrm{d}P + \Gamma \mathrm{d}\mu \qquad 3.61.1$$

where S_A^σ denotes S^σ/A.

From the equilibrium between the liquid phase, denoted by the superscript $^{\mathrm{L}}$, and the gas phase, denoted by the superscript $^{\mathrm{G}}$, we have as in §3.37

$$\mathrm{d}\mu = -S_\mathrm{m}^\mathrm{L}\mathrm{d}T + V_\mathrm{m}^\mathrm{L}\mathrm{d}P = -S_\mathrm{m}^\mathrm{G}\mathrm{d}T + V_\mathrm{m}^\mathrm{G}\mathrm{d}P. \qquad 3.61.2$$

When we eliminate $\mathrm{d}\mu$ and $\mathrm{d}P$ from (1) and (2) we obtain

$$-\mathrm{d}\gamma/\mathrm{d}T = (S_A^\sigma - \Gamma S_\mathrm{m}^\mathrm{L}) - (\tau - \Gamma V_\mathrm{m}^\mathrm{L})(S_\mathrm{m}^\mathrm{G} - S_\mathrm{m}^\mathrm{L})/(V_\mathrm{m}^\mathrm{G} - V_\mathrm{m}^\mathrm{L}). \qquad 3.61.3$$

This formula relates the temperature coefficient of the surface tension to certain entropy changes. Before we examine this formula in any detail, we shall show how it can be transformed to another relation involving energy changes instead of entropy changes.

For the two bulk phases we have as usual

$$\mu = G_\mathrm{m}^\mathrm{L} = U_\mathrm{m}^\mathrm{L} - TS_\mathrm{m}^\mathrm{L} + PV_\mathrm{m}^\mathrm{L} \qquad 3.61.4$$

$$\mu = G_\mathrm{m}^\mathrm{G} = U_\mathrm{m}^\mathrm{G} - TS_\mathrm{m}^\mathrm{G} + PV_\mathrm{m}^\mathrm{G}. \qquad 3.61.5$$

For the surface layer we have by applying to unit area the formulae of §1.56

$$\Gamma\mu = G_A^\sigma = U_A^\sigma - TS_A^\sigma + P\tau - \gamma \qquad 3.61.6$$

where G_A^σ denotes G^σ/A and U_A^σ denotes U^σ/A. We now use (4), (5), and (6) to eliminate S_m^L, S_m^G, and S^σ from (3). We obtain

$$\begin{aligned}-T\mathrm{d}\gamma/\mathrm{d}T = {} & (U_A^\sigma - \Gamma U_\mathrm{m}^\mathrm{L}) + P(\tau - \Gamma V_\mathrm{m}^\mathrm{L}) - \gamma \\ & - (\tau - \Gamma V_\mathrm{m}^\mathrm{L})(U_\mathrm{m}^\mathrm{G} - U_\mathrm{m}^\mathrm{L})/(V_\mathrm{m}^\mathrm{G} - V_\mathrm{m}^\mathrm{L}) - P(\tau - \Gamma V_\mathrm{m}^\mathrm{L}). \qquad 3.61.7\end{aligned}$$

The terms containing P cancel and (7) reduces to

$$\gamma - T\mathrm{d}\gamma/\mathrm{d}T = (U_A^\sigma - \Gamma U_\mathrm{m}^\mathrm{L}) - (\tau - \Gamma V_\mathrm{m}^\mathrm{L})(U_\mathrm{m}^\mathrm{G} - U_\mathrm{m}^\mathrm{L})/(V_\mathrm{m}^\mathrm{G} - V_\mathrm{m}^\mathrm{L}). \qquad 3.61.8$$

§3.62 *Invariance of relations*

We recall that according to the definition in §1.53 of a surface phase the properties associated with it depend on the position of the boundaries AA′ and BB′ in figure 1.2. We shall henceforth refer to these as the Lσ and the Gσ boundaries respectively. Since the precise placing of these boundaries is arbitrary, the values assigned to such quantities as τ, Γ, S^{σ}, U^{σ} are also arbitrary. We can nevertheless verify that our formulae are invariant with respect to shifts of either or both of the boundaries. It is hardly necessary to mention that the intensive variables T, P, and μ are unaffected by shifts of either boundary. It is also clear from the definition of γ in §1.58 that its value is invariant.

Let us now consider a shift of the plane boundary through a distance $\delta\tau$ away from the gas phase. Then Γ becomes increased by the amount of liquid in a cylinder of height $\delta\tau$ of cross-section unity and consequently of volume $\delta\tau$. Thus Γ becomes increased by $\delta\tau/V^{\mathrm{L}}_{\mathrm{m}}$. It follows immediately that $\tau-\Gamma V^{\mathrm{L}}_{\mathrm{m}}$ remains invariant. Similarly S^{σ}_{A} becomes increased by the entropy in a cylinder of liquid of volume $\delta\tau$ that is to say by an amount $S^{\mathrm{L}}_{\mathrm{m}}\delta\tau/V^{\mathrm{L}}_{\mathrm{m}}$. It follows immediately that $S^{\sigma}_{A}-\Gamma S^{\mathrm{L}}_{\mathrm{m}}$ remains invariant. Precisely similar considerations show that $U^{\sigma}_{A}-\Gamma U^{\mathrm{L}}_{\mathrm{m}}$ remains invariant.

We have now to consider a similar shift of the Gσ boundary through a distance $\delta\tau$ away from the liquid phase. Then Γ is increased by $\delta\tau/V^{\mathrm{G}}_{\mathrm{m}}$ and so $\tau-\Gamma V^{\mathrm{L}}_{\mathrm{m}}$ is increased by $(V^{\mathrm{G}}_{\mathrm{m}}-V^{\mathrm{L}}_{\mathrm{m}})\delta\tau$. Similarly $S^{\sigma}_{A}-\Gamma S^{\mathrm{L}}_{\mathrm{m}}$ is increased by $(S^{\mathrm{G}}_{\mathrm{m}}-S^{\mathrm{L}}_{\mathrm{m}})\delta\tau$. When we insert these values into (3.61.3) we see that the resulting variation vanishes. The same holds for (3.61.8).

§3.63 *Simplifying approximation*

The formulae of §3.61 are strictly accurate and involve no assumptions or approximations concerning the structure of the interfacial layer. We shall see that they can be greatly simplified by making use of our knowledge concerning this layer.

In §3.39 we mentioned that, at temperatures well below the critical, $PV^{\mathrm{L}}_{\mathrm{m}}$ is small compared with RT and may usually be ignored. In the interfacial layer the density is comparable to that in the liquid phase so that τ/Γ is comparable to $V^{\mathrm{L}}_{\mathrm{m}}$ and negligible compared with $V^{\mathrm{G}}_{\mathrm{m}}$. Consequently the terms containing the factor $\tau-\Gamma V^{\mathrm{L}}_{\mathrm{m}}$ may be neglected. Formulae (3.61.3) and (3.61.8) then reduce to, respectively,

$$-\mathrm{d}\gamma/\mathrm{d}\Gamma=S^{\sigma}_{A}-\Gamma S^{\mathrm{L}}_{\mathrm{m}} \qquad 3.63.1$$

$$\gamma-T\,\mathrm{d}\gamma/\mathrm{d}T=U^{\sigma}_{A}-\Gamma U^{\mathrm{L}}_{\mathrm{m}}. \qquad 3.63.2$$

It is worth noticing that the right side of (1) is the entropy of unit area of surface less the entropy of the same material content of liquid and the right side of (2) is the energy of unit area of surface less the energy of the same material content of liquid. More pictorially we may say that when unit area of surface is created isothermally and reversibly, the work done on the system is γ, the heat absorbed by the system is the right side of (1) multiplied by T, and the increase of energy, the sum of these two quantities, is equal to the right side of (2).

If however we are making the above simplifying approximations, then by making them at an earlier stage we can considerably simplify the derivations. We accordingly replace (3.61.1) by the approximation

$$-\mathrm{d}\gamma = S^{\sigma}_{A}\mathrm{d}T + \Gamma\mathrm{d}\mu \qquad 3.63.3$$

and (3.61.2) by the approximation

$$\mathrm{d}\mu = -S^{\mathrm{L}}_{\mathrm{m}}\mathrm{d}T = S^{\mathrm{G}}_{\mathrm{m}}\mathrm{d}T + RT\,\mathrm{d}\ln P. \qquad 3.63.4$$

Eliminating $\mathrm{d}\mu$ from (3) and (4) we obtain immediately

$$-\mathrm{d}\gamma = (S^{\sigma}_{A} - \Gamma S^{\mathrm{L}}_{\mathrm{m}})\mathrm{d}T \qquad 3.63.5$$

in agreement with (1).

Furthermore we replace (3.61.4) by the approximation

$$\mu = U^{\mathrm{L}}_{\mathrm{m}} - TS^{\mathrm{L}}_{\mathrm{m}} \qquad 3.63.6$$

and (3.61.6) by the approximation

$$\Gamma\mu = U^{\sigma}_{A} - TS^{\sigma}_{A} - \gamma. \qquad 3.63.7$$

Eliminating S^{σ}_{A} and $S^{\mathrm{L}}_{\mathrm{m}}$ from (5), (6), and (7) we recover (2).

We conclude this discussion with a warning against indiscriminately using the simplified formulae of this section in the neighbourhood of the critical point. The necessary condition for their use is that

$$\tau/\Gamma - V^{\mathrm{L}}_{\mathrm{m}} \ll V^{\mathrm{G}}_{\mathrm{m}} - V^{\mathrm{L}}_{\mathrm{m}}. \qquad 3.63.8$$

In the neighbourhood of the critical temperature $V^{\mathrm{L}}_{\mathrm{m}}$ becomes nearly as great as $V^{\mathrm{G}}_{\mathrm{m}}$ and this condition may no longer be taken for granted.

§3.64 *Vapour pressure of small drops*

Figure 3.14 represents a small spherical drop and a portion of liquid in bulk both at the same temperature. We denote the interiors of these liquid phases by α, β respectively and the vapour immediately outside them by

α', β' respectively. Let us assume that the external pressures $P^{\alpha'}$ and $P^{\beta'}$ are equal, that is

$$P^{\alpha'} = P^{\beta'}. \qquad 3.64.1$$

Then, according to (1.60.9) the pressure P^{α} at the interior α of the drop is greater than that P^{β} of the liquid in bulk by

$$P^{\alpha} - P^{\beta} = 2\gamma/a \qquad 3.64.2$$

where a is the radius of the drop. But according to (3.46.11) the fugacity p is related to the pressure P by

$$\mathrm{d}\ln p/\mathrm{d}P = V_{\mathrm{m}}^{\mathrm{L}}/RT. \qquad 3.64.3$$

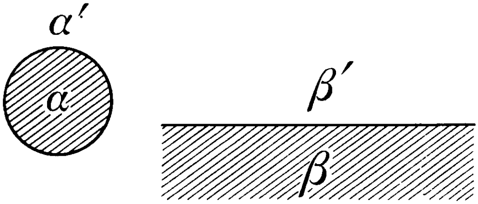

Fig. 3.14. Vapour pressure of droplet

If then we neglect the compressibility of the liquid, the fugacity p^{α} of the liquid in the drop is related to the fugacity p^{β} of the liquid in bulk by

$$RT\ln(p^{\alpha}/p^{\beta}) = (P^{\alpha} - P^{\beta})V_{\mathrm{m}}^{\mathrm{L}}. \qquad 3.64.4$$

Comparing (2) and (4) we find

$$RT\ln(p^{\alpha}/p^{\beta}) = 2\gamma V_{\mathrm{m}}^{\mathrm{L}}/a. \qquad 3.64.5$$

We see then that at the same external pressure the small drop always has a greater fugacity than the bulk liquid. Vapour will distil from the drop to the liquid and as the drop becomes smaller its fugacity increases still more. Thus small drops are essentially unstable relatively to the liquid in bulk.

§3.65 *Empirical temperature dependence of surface tension*

Since the surface tension of a liquid decreases with increasing temperature and vanishes at the critical point, the simplest possible form of empirical relation between γ and T is

$$\gamma = \gamma_0(1 - T/T_{\mathrm{c}})^{1+r} \qquad 3.65.1$$

where γ_0 and r are constants. For the substances having the simplest and most symmetrical molecules such as Ne, Ar, Xe, N_2, O_2 excellent agreement with the experimental data is obtained with $r=\frac{2}{9}$ as is shown in table 3.11. The data at the foot of this table will be discussed in §3.66.

The reason for the particular choice $r=\frac{2}{9}$ will be explained shortly. Ferguson* in a review of the experimental data for ten esters and four other organic compounds found $r=0.210\pm0.015$, which does not differ significantly from the value $\frac{2}{9}$ adopted above.

Another type of formula relates the surface tension to the coexisting proper volumes V^{L} of the liquid and V^{G} of the vapour. The simplest satisfactory formula of this type is the following

$$\gamma y^{-\frac{2}{3}} \propto (1-T/T_{\mathrm{c}}) \qquad 3.65.2$$

where y is defined in terms of densities ϱ by

$$y V_{\mathrm{c}} = (\varrho^{\mathrm{L}} - \varrho^{\mathrm{G}})/\varrho_{\mathrm{c}}. \qquad 3.65.3$$

This formula, due to Katayama†, is a striking improvement over the older and less accurate formula of Eötvos, which contained V^{L} instead of y^{-1}. This was shown by Katayama for various organic compounds and we shall now verify that this is also the case for the substances having the simplest molecules.

In §3.48 we verified that the substances having the simplest molecules follow with a high degree of accuracy formula (3.48.7), namely

$$(\varrho^{\mathrm{L}} - \varrho^{\mathrm{G}})/\varrho_{\mathrm{c}} = \tfrac{7}{2}(1-T/T_{\mathrm{c}})^{\frac{1}{3}}. \qquad 3.65.4$$

Using the definition (3) of y, this can be written

$$y \propto (1-T/T_{\mathrm{c}})^{\frac{1}{3}}. \qquad 3.65.5$$

If we now eliminate y between (2) and (5), we obtain

$$\gamma \propto (1-T/T_{\mathrm{c}})^{\frac{11}{9}} \qquad 3.65.6$$

of the form (1) with $r=\frac{2}{9}$. It follows that the verification of (6) in table 3.11 and the verification of (4) in figure 3.11 together constitute a verification of (2).

If instead of eliminating y between (2) and (5), we eliminate T/T_{c} between the same formulae we obtain

$$\gamma \propto y^{\frac{11}{3}}. \qquad 3.65.7$$

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* Ferguson, Trans. Faraday Soc. 1923 **19** 407; Proc. Phys. Soc. London 1940 **52** 759.

† Katayama, Sci. Rep. Tôhoku Univ. 1916 **4** 373.

TABLE 3.11

$$\gamma=\gamma_0(1-T/T_c)^{\frac{11}{9}}$$

Ne			Ar			Xe			N_2			O_2		
$T_c=44.8$ K $\gamma_0=15.1$ dyne cm^{-1}			$T_c=150.7$ K $\gamma_0=36.31$ dyne cm^{-1}			$T_c=289.8$ K $\gamma_0=50.70$ dyne cm^{-1}			$T_c=126.0$ K $\gamma_0=28.4$ dyne cm^{-1}			$T_c=154.3$ K $\gamma_0=38.4$ dyne cm^{-1}		
T/K	γ/dyne cm^{-1}		T/K	γ/dyne cm^{-1}		T/K	γ/dyne cm^{-1}		T/K	γ/dyne cm^{-1}		T/K	γ/dyne cm^{-1}	
	calc.	obs.		calc.	obs.		calc.	obs.		calc.	obs.		calc.	obs.
24.8	5.64	5.61	85.0	13.16	13.19	162	18.7	18.7	70.0	10.54	10.53	70.0	18.34	18.35
25.7	5.33	5.33	87.0	12.67	12.68	164	18.3	18.3	75.0	9.40	9.39	75.0	17.02	17.0
26.6	5.02	4.99	90.0	11.95	11.91				80.0	8.29	8.27	80.0	15.72	15.73
27.4	4.75	4.69							85.0	7.20	7.20	85.0	14.44	14.5
28.3	4.45	4.44							90.0	6.14	6.16	90.0	13.17	13.23
$V_c=41.7$ cm^3 mole^{-1} $\gamma_0 V_c^{\frac{2}{3}} T_c^{-1}=$ 4.05 erg K^{-1}mole$^{-\frac{2}{3}}$			$V_c=75.3$ cm^3 mole^{-1} $\gamma_0 V_c^{\frac{2}{3}} T_c^{-1}=$ 4.3 erg K^{-1}mole$^{-\frac{2}{3}}$			$V_c=118.8$ cm^{3}mole^{-1} $\gamma_0 V_c^{\frac{2}{3}} T_c^{-1}=$ 4.2 erg K^{-1}mole$^{-\frac{2}{3}}$			$V_c=90.2$ cm^{3}mole^{-1} $\gamma_0 V_c^{\frac{2}{3}} T_c^{-1}=$ 4.5 erg K^{-1}mole$^{-\frac{2}{3}}$			$V_c=74.5$ cm^{3}mole^{-1} $\gamma_0 V_c^{\frac{2}{3}} T_c^{-1}=$ 4.4 erg K^{-1}mole$^{-\frac{2}{3}}$		

The better known relation of Macleod* with an index 4 instead of $\frac{11}{3}$ is less accurate, at least for the substances having the simplest molecules. Actually for the half dozen organic compounds considered by Macleod it is clear that γ in fact varies as some power of y less than 4.

§3.66 *Corresponding states of surface tension*

The principle of corresponding states, so far as it is applicable at all to surfaces, can on physical grounds be expected to hold only for subtances having the simplest and most symmetrical molecules.

According to the principle it is clear from dimensional considerations that $\gamma V_c^{\frac{2}{3}} T_c^{-1}$ should be a common function of T/T_c for substances obeying the principle. In particular, if these substances obey (3.65.1) then $\gamma_0 V_c^{\frac{2}{3}} T_c^{-1}$ should have a common value. The data† at the bottom of table 3.11 show that this is in fact the case within about ± 2% for Ar, Xe, N_2, O_2 while the value for Ne deviates by rather less than 10%.

More recent measurements‡ are summarized in table 3.12.

TABLE 3.12

	Ar	N_2	CH_4
γ_0/dyne cm^{-1}	37.78	28.12	39.08
$\gamma_0 V_c^{\frac{2}{3}} T_c^{-1}$/erg K^{-1} mole$^{-\frac{2}{3}}$	4.25	4.48	4.39

§3.67 *Sorption of a single gas*

In our discussion of the interface between a liquid and a gas the surface area A was first introduced as an independent variable. The interfacial tension γ was then introduced through the relation

$$w = \gamma \mathrm{d}A. \qquad 3.67.1$$

Both A and γ are well defined measurable quantities. The situation for a solid–gas interface is altogether different. The area of the interface may be difficult, if not impossible, to measure accurately especially if the solid is porous or a powder. Furthermore the surface area can not be varied reversibly and consequently there is no relation such as (1). There is no quantity

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[*] Macleod, Trans. Faraday Soc. 1923 **19** 38.

[†] Guggenheim, J. Chem. Phys. 1945 **13** 259. Guggenheim, Proc. Phys. Soc. London 1965 **85** 811.

[‡] Sprow and Prausnitz, Trans. Faraday Soc. 1966 **62** 1102.

analogous to interfacial tension. For discussing the equilibrium between a gas and a solid–gas interface a completely different approach is called for.

The name *sorption* was coined by McBain* to include as special cases absorption and adsorption which should be restricted to proven cases of solution and surface condensation respectively.

In the following discussion of sorption we shall assume that the sorbed gas is a single substance, but no restriction will be placed on the nature of the sorbent except that we assume absence of hysteresis. In other words we shall consider the equilibrium between a single gas and a sorbent which may be a piece of platinum gauze, a lump of impure charcoal, or some powdered glass, or in fact almost anything.

The first question to be considered is how to measure sorption. This may be done by a sorption balance. Essentially the sorbent is suspended on a spring balance so that its weight, and thence its mass, can be compared in vacuo and in equilibrium with a surrounding gas at a given temperature and pressure. If no correction is applied for the buoyancy due to the surrounding gas, the apparent increase in mass recorded by the balance is equal to that of the excess quantity of the sorbed substance due to sorption over and above the quantity which would be contained in the same volume, at the same temperature and pressure, in the absence of the sorbent. This mass divided by the proper mass of the gas is equal to the excess amount of the sorbed substance due to sorption over and above the amount of the gas which would be contained in the same volume, at the same temperature and pressure, in the absence of the sorbent. We denote this amount by n^{a} and we shall call n^{a} the sorbed excess. This quantity is the simplest and most convenient measure of sorption. At a first approach it might seem that a simpler quantity would be the amount of sorbed substance contained by the sorbent. Such a quantity would have to be calculated by adding to n^{a} the quantity $\varrho V^{\mathrm{s}}/M$ where ϱ is the density of the gas, M is the proper mass of the gas, and V^{s} is the volume of the sorbent. On reflection it becomes clear that V^{s} is a rather vague quantity, difficult if not impossible to measure accurately especially if the sorbent is porous or a powder. This difficulty is completely avoided by using n^{a}, without any buoyancy correction as our measure of sorption. We shall adopt this approach and shall consider how n^{a} is related to the temperature and pressure.

§3.68 *Temperature dependence of sorption*

We consider a vessel of volume V containing the sorbent and a fixed amount

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* McBain, Phil. Mag. 1909 **18** 916.

n of the sorbate at the temperature T and pressure P. If V_{m} denotes the proper volume of gaseous sorbate, then according to the definition of n^{a} in the previous section we have

$$V=(n-n^{\mathrm{a}})V_{\mathrm{m}}. \tag{3.68.1}$$

We now combine Maxwell's relation (1.47.4) with (1) and obtain

$$-(\partial S/\partial P)_T=(\partial V/\partial T)_P=(n-n^{\mathrm{a}})(\partial V_{\mathrm{m}}/\partial T)_P-(\partial n^{\mathrm{a}}/\partial T)_P V_{\mathrm{m}} \tag{3.68.2}$$

and consequently

$$\begin{aligned}-(\partial S/\partial n^{\mathrm{a}})_T &= -(\partial S/\partial P)_T(\partial P/\partial n^{\mathrm{a}})_T\\ &=(n-n^{\mathrm{a}})(\partial V_{\mathrm{m}}/\partial T)_P(\partial P/\partial n^{\mathrm{a}})_T-(\partial n^{\mathrm{a}}/\partial T)_P V_{\mathrm{m}}(\partial P/\partial n^{\mathrm{a}})_T\\ &=(n-n^{\mathrm{a}})(\partial V_{\mathrm{m}}/\partial T)_P(\partial P/\partial n^{\mathrm{a}})_T+(\partial P/\partial T)_{n^{\mathrm{a}}} V_{\mathrm{m}}.\end{aligned} \tag{3.68.3}$$

We now compare our system with another system consisting of a vessel of the same volume V containing the same gas at the same temperature and pressure but without any sorbent. We shall use dashed symbols for quantities relating to this second system when they may differ from those relating to the first system. We have then

$$n'=n-n^{\mathrm{a}}. \tag{3.68.4}$$

Moreover since both systems are in equilibrium and the gas is in identical conditions we have also

$$\mu'=\mu. \tag{3.68.5}$$

If now we denote by ΔS_{m} the entropy increase in the first system per unit decrease of n^{a} brought about by decreasing the pressure, we have according to (3)

$$\Delta S_{\mathrm{m}}=(n-n^{\mathrm{a}})(\partial V_{\mathrm{m}}/\partial T)_P(\partial P/\partial n^{\mathrm{a}})_T+(\partial P/\partial T)_{n^{\mathrm{a}}} V_{\mathrm{m}}. \tag{3.68.6}$$

If further we denote by $\Delta' S$ the entropy increase in the second system corresponding to the same decrease in pressure, we have

$$\Delta' S_{\mathrm{m}}=n'(\partial V_{\mathrm{m}}/\partial T)_P(\partial P/\partial n^{\mathrm{a}})_T. \tag{3.68.7}$$

Subtracting (7) from (6) and using (4) we obtain

$$\Delta S_{\mathrm{m}}-\Delta' S_{\mathrm{m}}=(\partial P/\partial T)_{n^{\mathrm{a}}} V_{\mathrm{m}} \tag{3.68.8}$$

or

$$T\Delta S_{\mathrm{m}}-T\Delta' S_{\mathrm{m}}=T(\partial P/\partial T)_{n^{\mathrm{a}}} V_{\mathrm{m}}. \tag{3.68.9}$$

It follows immediately from (5) that

$$\Delta\mu=\Delta'\mu \tag{3.68.10}$$

and so subtracting (10) from (9) we obtain the alternative formula

$$\Delta H_{\mathrm{m}} - \Delta' H_{\mathrm{m}} = T(\partial P/\partial T)_{n^{\mathrm{a}}} V_{\mathrm{m}}. \qquad 3.68.11$$

The left side of either (9) or (11) may be called* the *equilibrium proper enthalpy of desorption.* It is the heat that must be supplied per unit decrease of n^{a} resulting from decrease of pressure under isothermal equilibrium conditions less the heat that must be supplied to the second system when the pressure is isothermally decreased by the same amount. We emphasize that every quantity occurring in (9) and (11) is experimentally determinable without the use of any approximation or extraneous assumption. This contrasts with some other formulae which contain quantities such as the surface area of the sorbent, the spreading pressure, and the volume occupied by a sorbed molecule. Such quantities play their natural part as parameters in a model used for a kinetic or statistical mechanical theory of sorption, but, not being accurately measurable, they have no part in a treatment by classical thermodynamics.

In all normal applications the pressure will be sufficiently small to justify neglect of all virial coefficients higher than the second. We then have in accordance with (3.19.5)

$$V_{\mathrm{m}} = RT/P + B. \qquad 3.68.12$$

Substituting (12) into (9) and (11) we obtain

$$T\Delta S_{\mathrm{m}} - T\Delta' S_{\mathrm{m}} = \Delta H_{\mathrm{m}} - \Delta' H_{\mathrm{m}} = RT^2(\partial \ln P/\partial T)_{n^{\mathrm{a}}}(1 + PB/RT). \qquad 3.68.13$$

When the term in B is negligible so that the gas is effectively perfect, (13) reduces to a form derivable by more elementary methods.

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* The derivation of these formulae was presented to the Boston University Conference on Nucleation 1951.