CHAPTER 6

SYSTEMS OF CHEMICALLY REACTING SPECIES

§6.01 *Notation and terminology*

Any chemical process may be written in the form

$$\sum_{\mathrm{A}} \nu_{\mathrm{A}}\,\mathrm{A} \rightarrow \sum_{\mathrm{B}} \nu_{\mathrm{B}}\,\mathrm{B} \qquad 6.01.1$$

where A, B denote chemical species and ν_{A}, ν_{B} are integers or simple rational fractions. Since the meaning of formula (1) has sometimes been misunderstood it is desirable to state unambiguously what it means and what it does not. It means that in a system containing a large amount of A,…, B,… the amounts reacting are $\nu_{\mathrm{A}}, \ldots, \nu_{\mathrm{B}}, \ldots$. It does not mean that a system composed of an amount ν_{A} of A,…, is changed completely into an amount ν_{B} of B,….

We can measure the extent to which the process (1) takes place by the *extent of reaction* defined in §1.44 such that a change of ξ to $\xi + \mathrm{d}\xi$ means that an amount $\nu_{\mathrm{A}}\mathrm{d}\xi$ of A and the like react to given an amount $\nu_{\mathrm{B}}\mathrm{d}\xi$ of B and the like. We also recall that the *affinity* of the reaction is defined as

$$-(\partial \mathcal{F}/\partial \xi)_{T,V} = -(\partial G/\partial \xi)_{T,P^{\alpha}} \qquad 6.01.2$$

where P^{α} is the pressure of each phase α.

If ξ increases by $\mathrm{d}\xi$ in a time $\mathrm{d}t$ we then have the concise universal law that in any natural process

$$-(\partial G/\partial \xi)_{T,P^{\alpha}}\mathrm{d}\xi/\mathrm{d}t > 0 \qquad \text{(natural)} \qquad 6.01.3$$

and consequently for equilibrium

$$-(\partial G/\partial \xi)_{T,P^{\alpha}} = 0 \qquad \text{(equilibrium).} \qquad 6.01.4$$

Formula (4) is equivalent to

$$\sum_{\mathrm{A}} \nu_{\mathrm{A}}\mu_{\mathrm{A}} = \sum_{\mathrm{B}} \nu_{\mathrm{B}}\mu_{\mathrm{B}} \qquad \text{(equilibrium).} \qquad 6.01.5$$

We now recall the abbreviated notation described in §1.44 according to which we replace (1) by

$$0=\sum_{\mathrm{B}} \nu_{\mathrm{B}}\mathrm{B} \qquad 6.01.6$$

where now each ν_{B} is negative for a reactant and positive for a reaction product. In this abbreviated notation (5) becomes

$$\sum_{\mathrm{B}} \nu_{\mathrm{B}}\mu_{\mathrm{B}}=0. \qquad 6.01.7$$

Since the absolute activity is related to the chemical potential by

$$\mu=RT \ln \lambda \qquad 6.01.8$$

formula (7) is equivalent to

$$\prod_{\mathrm{B}} (\lambda_{\mathrm{B}})^{\nu_{\mathrm{B}}}=1 \qquad \text{(equilibrium).} \qquad 6.01.9$$

We shall now further abbreviate our notation. Let I_{B} denote any intensive property relating to the species B such as λ_{B}, p_{B}, x_{B}, r_{B}, m_{B}, γ_{B}. Then we shall use the contracted notation $\Pi(I)$ defined by

$$\prod(I)=\prod_{\mathrm{B}} (I_{\mathrm{B}})^{\nu_{\mathrm{B}}}. \qquad 6.01.10$$

When the I_{B}'s have values corresponding to a state of chemical equilibrium we shall call $\Pi(I)$ the *equilibrium product* of the I_{B}'s.

Our first application of this notation is to (9) which we contract to

$$\prod(\lambda)=1 \qquad \text{(equilibrium)} \qquad 6.01.11$$

and the general condition for chemical equilibrium may be stated as: *the equilibrium product of the absolute activities* is unity.

§6.02 *Enthalpy of reaction*

Consider the constant temperature process

$$0=\sum_{\mathrm{B}} \nu_{\mathrm{B}}\mathrm{B} \qquad (T \text{ const.}) \qquad 6.02.1$$

and let the operator Δ denote the excess of a final over an initial value corresponding to unit increase in the extent of reaction. If the process occurs at constant pressure then the heat absorbed is equal to ΔH. For this reason ΔH is called either the *heat of reaction at constant pressure* or better the *enthalpy of reaction.*

If on the other hand the process occurs at constant volume the heat absorbed is equal to ΔU, which is therefore called the *heat of reaction* *at constant volume.* This quantity is of little importance except for reactions involving a gas phase, for which it is related to ΔH by

$$\Delta U = \Delta H - RT \sum_{\mathrm{B}}{}' \nu_{\mathrm{B}} \qquad 6.02.2$$

where Σ' denotes summation over gaseous species only, the second virial coefficients and proper volumes of condensed phases being neglected.

We recall that for a perfect gas H is independent of the pressure and for a condensed phase the effect of variations of pressure is negligible. It is therefore often unnecessary to specify the pressure when speaking of enthalpies of reaction.

§6.03 *Hess' law*

Since H is a function of the state of a system, ΔH is for successive processes at the same temperature an additive function. This property of ΔH, known as *Hess' law*, is useful in enabling us to calculate ΔH for a reaction, difficult to produce quantitatively, from other reactions which give less difficulty. The following simple example illustrates the point

$$\mathrm{C(graphite)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \qquad -\Delta H = 393.5\ \mathrm{kJ}$$
$$\mathrm{CO(g)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \qquad -\Delta H = 283.0\ \mathrm{kJ}.$$

In both the above cases ΔH is readily measurable. By subtraction we obtain

$$\mathrm{C(graphite)} + \tfrac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO(g)} \qquad -\Delta H = 110.5\ \mathrm{kJ}$$

a reaction difficult, if not impossible, to study quantitatively.

Other numerous examples are the calculations of the *enthalpies of formation* of organic compounds from the *enthalpies of combustion.* A simple example is

$$\mathrm{CH_4(g)} + 2\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} + 2\mathrm{H_2O(l)} \qquad -\Delta H = 890.3\ \mathrm{kJ}$$
$$\mathrm{C(graphite)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \qquad -\Delta H = 393.5\ \mathrm{kJ}$$
$$2\mathrm{H_2(g)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{H_2O(l)} \qquad -\Delta H = 571.6\ \mathrm{kJ}$$

from which we immediately deduce

$$\mathrm{C(graphite)} + 2\mathrm{H_2(g)} \rightarrow \mathrm{CH_4(g)} \qquad -\Delta H = 74.8\ \mathrm{kJ}.$$

Unfortunately in calculating an enthalpy of formation as the difference between much greater enthalpies of combustion there is considerable loss in percentage accuracy since the experimental errors add up. Nevertheless this is the standard method for determining enthalpies of formation of organic compounds from their elements.

Unfortunately some authors have used the name *heat of reaction* for $-\Delta H$ instead of for ΔH. This practice is deplorable. In particular the name 'heat of combustion' is commonly used for $-\Delta H$. It might be pleaded in excuse that in this case $-\Delta H$ is always positive and that there is no other convenient name. There is on the other hand no excuse whatever for the habit of calling $-\Delta H$ for adsorption a 'heat of adsorption' when there exists the perfectly good name *heat of desorption*. The simplest and safest way to avoid any possible ambiguity is to write explicitly $\Delta H = \ldots$ or $-\Delta H = \ldots$ as in the above examples.

§6.04 *Kirchhoff's relations*

We often need the value of ΔH at one temperature when it has been measured at a different temperature. This causes no difficulty provided the dependence of H on the temperature has been measured or is known theoretically for the initial and final states.

Let T denote the temperature at which we want the value of ΔH and T' the temperature at which it has been measured. Then

$$\Delta H(T) - \Delta H(T') = \sum_{\mathrm{B}} \nu_{\mathrm{B}} H_{\mathrm{B}}(T) - \sum_{\mathrm{B}} \nu_{\mathrm{B}} H_{\mathrm{B}}(T') = \sum_{\mathrm{B}} \nu_{\mathrm{B}} \{H_{\mathrm{B}}(T) - H_{\mathrm{B}}(T')\}. \qquad 6.04.1$$

Although (1) is the form in which the experimental data are available and should be used, it is customary to express it in the differential form

$$\mathrm{d}\Delta H/\mathrm{d}T = \sum_{\mathrm{B}} \nu_{\mathrm{B}} \mathrm{d}H_{\mathrm{B}}/\mathrm{d}T = \sum_{\mathrm{B}} \nu_{\mathrm{B}} C_{\mathrm{B}}. \qquad 6.04.2$$

Formula (2) is known as *Kirchhoff's relation*. Since values of the heat capacities C are usually obtained by differentiating experimental measurements of $H(T) - H(T')$ and formula (2), if used, has to be integrated, it is difficult to see any advantage of (2) over (1). As already mentioned in §3.03 the main function of a heat capacity is to serve as the connecting link between the enthalpy and the entropy.

There is a second formula also associated with Kirchhoff, similar to (2), but relating the energy change ΔU with the heat capacities at constant volume, but this formula is not needed.

§6.05 *Prescription of standards*

As already explained in §3.25 the formulae for chemical equilibrium require a consistent choice of standards $P^{\ominus}$, $\lambda^{\ominus}$, $H^{\ominus}$, and $S^{\ominus}$. We now prescribe the choice used almost universally and used henceforth in this text.

The standard pressure $P^\ominus$ is prescribed as

$$P^\ominus = 1 \text{ atm}. \qquad 6.05.1$$

The standard enthalpy is prescribed by stating that

$$H^\ominus = 0 \qquad (T = 298.15 \text{ K}) \qquad 6.05.2$$

for every *element in its stable state.* The standard entropy is prescribed by stating that

$$S^\ominus = 0 \qquad (T \to 0) \qquad 6.05.3$$

for every *element in its stable state.*

Since $H^\ominus(T) - H^\ominus(298.15 \text{ K})$ is determinable by purely calorimetric measurements, the convention expressed by (2) determines unambiguously the value of $H^\ominus(T)$ for any T. Similarly since $S^\ominus(T) - S^\ominus(0)$ is determinable by purely calorimetric measurements, the convention expressed by (3) determines unambiguously the value of $S^\ominus(T)$ for any T. Then $\lambda^\ominus$ is unambiguously defined by

$$\ln \lambda^\ominus = H^\ominus/RT - S^\ominus/R. \qquad 6.05.4$$

Extensive tables exist of values of $H^\ominus(298.15 \text{ K})$ and of $S^\ominus(298.15 \text{ K})$. Less extensive tables exist of $H^\ominus(T)$ and of $S^\ominus(T)$ for other values of T.

Most of these tables give values of $H^\ominus$ in kcal mole^{-1} and of $S^\ominus$ in cal K^{-1} mole^{-1} although all precise calorimetric measurements are made in terms of joules. It would save considerable unnecessary calculation if the tabulated quantities were $H^\ominus/R$ and $S^\ominus/R$.

§6.06 *Construction of tables*

As already mentioned extensive tables exist of values of $H^\ominus$ and of $S^\ominus$ for $T = 298.15$ K. We now summarize briefly how these are constructed. We begin with $H^\ominus$.

The first step in determining $H^\ominus$ for a given substance is to choose a set of reactions for which the enthalpy of reaction can be measured directly and which add up to the process of formation of the given substance from its elements. Two simple examples have already been mentioned in §6.03. The set of reactions may include isothermal changes of pressure so as to convert each measured ΔH to the required $\Delta H^\ominus$. The values of the enthalpies of reaction at the several experimental temperatures are reduced to values at 298.15 K by use of Kirchhoff's relation. The values at 298.15 K for the several reactions are combined according to Hess' law to obtain the heat of formation $\Delta_f H^\ominus$. Finally from the chosen convention that $H^\ominus$ at 298.15 K is zero for every element in its stable state it follows that for each compound $H^{\ominus} = \Delta_f H^{\ominus}$ and this is the quantity tabulated. In the most extensive tables* $H^{\ominus}(298.15\text{ K})$ is denoted by ΔHf^0.

We now consider the tabulation of $S^{\ominus}$. Purely calorimetric measurements, as illustrated in §3.52, lead directly to $S^{\ominus}(298.15\text{ K}) - S^{\ominus}(\text{crystal}, T \to 0)$. When we choose the convention that $S^{\ominus}(T \to 0)$ is zero for every element in its stable crystalline form we have for any substance

$$S^{\ominus}(\text{crystal}, T \to 0) = R \ln o \qquad 6.06.1$$

and consequently

$$S^{\ominus}(298.15\text{ K}) = \{S^{\ominus}(298.15\text{ K}) - S^{\ominus}(\text{crystal}, T \to 0)\} + R \ln o. \qquad 6.06.2$$

The expression { } is often called the *calorimetric entropy*. In order to determine the tabulated quantity $S^{\ominus}(298.15\text{ K})$ we need to know or assume the value of o. There are three different possibilities. For about thirty substances with simple molecules $S^{\ominus}(298.15\text{ K})$ for the gas has been determined from purely spectroscopic data and this value, often called the *spectroscopic entropy*, is found to be equal to the *calorimetric entropy*. It follows for all these substances that $o = 1$ or $\ln o = 0$. For a few substances with simple molecules, namely CO, N_2O, NO, H_2O the spectroscopic entropy is found to exceed the calorimetric entropy by amounts $R \ln 2$, $R \ln 2$, $\frac{1}{2}R \ln 2$, $R \ln \frac{3}{2}$ so that o has values differing from unity. These non-zero values of $\ln o$ are understood and have been explained in §3.54. In each case they are due to metastability in the crystal. Finally for all other substances the value of o has not been determined experimentally. Its value is assumed to be unity. It is conceivable that there are other cases of $o > 1$ but they are likely to be few if any. The use of the assumption $o = 1$ can thus conceivably lead to equilibrium constants wrong by a factor such as 2. In the most extensive tables* $S^{\ominus}(298.15\text{ K})$ is denoted by S^0.

Tables† less extensive than those for 298.15 K exist relating to other temperatures. These tables give values of the purely calorimetric quantities $H^{\ominus}(T) - H^{\ominus}(298.15\text{ K})$ and $S^{\ominus}(T) - S^{\ominus}(298.15\text{ K})$.

§6.07 *Gaseous equilibria*

For every component B in a gas phase we have according to (4.08.1)

$$\lambda_B = \lambda_B^{\ominus} p_B / P^{\ominus} \qquad 6.07.1$$

where p_B is the fugacity of B, $P^{\ominus}$ is a standard pressure, normally one

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* Rossini et al., Circular no. 500 of National Bureau of Standards, 1952.

† Kelley, U.S. Bureau of Mines, 1949, Bulletin 476.

atmosphere, and $\lambda_B^\ominus$ is the value of λ_B when p_B is equal to $P^\ominus$. Substituting (1) into (6.01.11) we obtain the equilibrium condition

$$\prod(p)=K \qquad 6.07.2$$

where K is a function of temperature only defined by

$$K=\prod(P^\ominus/\lambda^\ominus) \qquad 6.07.3$$

and is called the *equilibrium constant.* Lack of experimental data on virial coefficients in gaseous mixtures usually makes it impossible to correct for gas imperfection, even though the procedure is in principle straightforward. When we adopt the approximation

$$p_B=x_BP \qquad \text{(perfect gas)} \qquad 6.07.4$$

(2) becomes

$$\prod(xP)=K. \qquad 6.07.5$$

We may rewrite (5) as

$$\prod(x)=K_x \qquad \text{(perfect gas)} \qquad 6.07.6$$

where

$$K_x=K/\prod(P) \qquad 6.07.7$$

so that K_x as well as depending on the temperature is inversely proportional to $P^{\Sigma\nu_B}$. There is no advantage in using K_x instead of K.

§6.08 *Equilibria between gases and solids*

We turn now to a discussion of the equilibrium of reactions involving pure solids as well as gases. Examples are

$$CaCO_3(s)\rightarrow CaO(s)+CO_2(g) \qquad 6.08.1$$

$$NH_4Cl(s)\rightarrow NH_3(g)+HCl(g) \qquad 6.08.2$$

$$C(graphite)+CO_2(g)\rightarrow 2CO(g). \qquad 6.08.3$$

We have the general equilibrium condition (6.01.11)

$$\prod(\lambda)=1 \qquad 6.08.4$$

where the λ of each gaseous species is related to its fugacity by (6.07.1). On the other hand we may regard the λ of each pure solid as a function of temperature only, since the effect of change of pressure on a solid is usually negligible.

We now extend our Π notation as follows. We write

$$\prod(l)=\prod_G(l)\prod_S(l) \qquad 6.08.5$$

where $\Pi_G(I)$ contains all the factors of $\Pi(I)$ relating to the gaseous species and $\Pi_S(I)$ all the factors relating to the solid species.

For example in the case of reaction (1)

$$\prod_G (\lambda) = \lambda_{CO_2} \tag{6.08.6}$$

$$\prod_S (\lambda) = \lambda_{CaO}/\lambda_{CaCO_3}\,. \tag{6.08.7}$$

Using this notation, the equilibrium condition (4) may be written

$$\prod_G (\lambda) \prod_S (\lambda) = 1. \tag{6.08.8}$$

Now substituting (6.07.1) into (8) we obtain

$$\prod_G (p) = K \tag{6.08.9}$$

where K is a function of temperature only given by

$$K = \prod_G (P^\ominus/\lambda^\ominus) \prod_S (1/\lambda^\ominus) \tag{6.08.10}$$

and is called the *equilibrium constant*. For example for reaction (3), we have

$$p^2_{CO}/p_{CO_2} = \mathrm{K} \tag{6.08.11}$$

$$K = \lambda^\ominus_{CO_2} \lambda^\ominus_C P^\ominus/\lambda^{\ominus 2}_{CO}. \tag{6.08.12}$$

§6.09 *Temperature dependence*

For any reaction

$$0 = \sum_B \nu_B \mathrm{B} \tag{6.09.1}$$

between gases and solids, or between gases only, the equilibrium constant K is given by (6.08.10)

$$K = \prod_G (P^\ominus/\lambda^\ominus) \prod_S (1/\lambda^\ominus). \tag{6.09.2}$$

For each species B whether gaseous or solid we have

$$\mathrm{d} \ln \lambda^\ominus_B/\mathrm{d}T = -H^\ominus_B/RT^2. \tag{6.09.3}$$

Taking logarithms and differentiating (2) with respect to T and using (3) we obtain

$$\mathrm{d} \ln K/\mathrm{d}T = \sum_B H^\ominus_B/RT^2 = \Delta H^\ominus/RT^2 \tag{6.09.4}$$

where $\Delta H^\ominus$ is the standard enthalpy of reaction. This may be written in the alternative form

$$\mathrm{d} \ln K/\mathrm{d}(1/T) = -\sum_B H^\ominus_B/R = -\Delta H^\ominus/R. \tag{6.09.5}$$

§6.10 *Numerical example*

We shall now illustrate the use of our formulae and of standard tables by a simple example. We choose the reaction

$$0 = 2\mathrm{CO(g)} - \mathrm{C(graphite)} - \mathrm{CO_2(gas)} \quad \text{at } 1000\ \mathrm{K}. \qquad 6.10.1$$

The equilibrium is determined by

$$p_{\mathrm{CO}}^2 / p_{\mathrm{CO_2}} = K \qquad 6.10.2$$

where

$$K = P^{\ominus} \lambda_{\mathrm{CO_2}}^{\ominus} \lambda_{\mathrm{C}}^{\ominus} / \lambda_{\mathrm{CO}}^{\ominus 2} = (\lambda_{\mathrm{CO_2}}^{\ominus} \lambda_{\mathrm{C}}^{\ominus} / \lambda_{\mathrm{CO}}^{\ominus 2})\ \mathrm{atm}. \qquad 6.10.3$$

The tabulated experimental data* are as follows

B	C(graphite)	$\mathrm{CO_2(g)}$	CO(g)	$\sum_{\mathrm{B}}$
ν_{B}	-1	-1	$+2$	
$H_{\mathrm{B}}^{\ominus}(25\ °\mathrm{C})/\mathrm{kcal\ mole^{-1}}$	0	-94.05	-26.42	
$S_{\mathrm{B}}^{\ominus}(25\ °\mathrm{C})/\mathrm{cal\ K^{-1}\ mole^{-1}}$	1.36	51.06	47.30	
$H_{\mathrm{B}}^{\ominus}(1000\ \mathrm{K}) - H_{\mathrm{B}}^{\ominus}(25\ °\mathrm{C})/\mathrm{kcal\ mole^{-1}}$	2.810	7.993	5.186	
$S_{\mathrm{B}}^{\ominus}(1000\ \mathrm{K}) - S_{\mathrm{B}}^{\ominus}(25\ °\mathrm{C})/\mathrm{cal\ K^{-1}\ mole^{-1}}$	4.47	13.28	8.82	
$H_{\mathrm{B}}^{\ominus}(1000\ \mathrm{K})/\mathrm{kcal\ mole^{-1}}$	2.810	-86.059	-21.230	40.789
$S_{\mathrm{B}}^{\ominus}(1000\ \mathrm{K})/\mathrm{cal\ K^{-1}\ mole^{-1}}$	5.83	64.34	56.12	42.07

From these we deduce

$$\ln(K/\mathrm{atm}) = -\Delta H^{\ominus}/RT + \Delta S^{\ominus}/R = (42.07 - 40.79)/1.987 = 0.64$$

$$K = 1.9\ \mathrm{atm}.$$

The accuracy of a calculation of this kind is at best about ±0.05 in each term of $\ln K$. This usually leads to an uncertainty of at least 0.1 in $\ln K$ or 10% in K. In most cases the experimental uncertainty in a direct measurement of K is no less.

§6.11 *Reactions between pure solids or liquids*

We must now consider reactions between pure solid phases without any gases. Examples are

$$0 = \mathrm{PbI_2} - \mathrm{Pb} - 2\mathrm{I} \qquad 6.11.1$$

$$0 = \mathrm{CuS} - \mathrm{Cu} - \mathrm{S}. \qquad 6.11.2$$

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* Rossini et al., Circular no. 500 of National Bureau of Standards, 1952.

Incidentally, for the following considerations it is immaterial whether any of the phases is a pure liquid instead of a pure solid. As an example we may mention

$$0 = \mathrm{Ag} + \mathrm{HgCl} - \mathrm{Hg} - \mathrm{AgCl}. \qquad 6.11.3$$

The simplest type of reaction between solid phases is an allotropic change, such as

$$0 = \text{monoclinic sulphur} - \text{rhombic sulphur} \qquad 6.11.4$$

$$0 = \text{white tin} - \text{grey tin}. \qquad 6.11.5$$

The equilibrium condition for a reaction involving pure solid and liquid phases can still be expressed in the form (6.01.11)

$$\prod(\lambda) = 1 \qquad \text{(equilibrium)} \qquad 6.11.6$$

but each λ is now a function of temperature only, if we disregard the small effect of changes of pressure. Hence the equilibrium condition (6) may be regarded as an equation determining the temperature of reversal of the change considered. This equation may or may not have a solution for T positive. Reactions (1), (2), (3) proceed naturally towards the right at all temperatures and there is no solution of (6). In point of fact very few reactions between pure solids and pure liquids have a reversal temperature. The most important exceptions are allotropic changes such as (4) and (5), among which we may, if we like, include simple fusion.

For reactions such as (1), (2), (3) at all temperatures we have

$$\prod(\lambda) < 1 \qquad 6.11.7$$

or taking logarithms and writing in full,

$$\sum_{\mathrm{B}} \nu_{\mathrm{B}} \ln \lambda_{\mathrm{B}} < 0. \qquad 6.11.8$$

Another way of expressing the same thing is to state that the affinity, defined in §1.44, is positive at all temperatures. We shall see in chapter 8 how the affinity of some reactions can be accurately determined by measurements of electromotive force.

We shall now consider (6) in more detail and for this purpose we write it in the expanded form

$$\sum_{\mathrm{B}} \nu_{\mathrm{B}} \ln \lambda_{\mathrm{B}} = 0. \qquad 6.11.9$$

But by definition

$$\ln \lambda_{\mathrm{B}} = \mu_{\mathrm{B}}/RT = H_{\mathrm{B}}/RT - S_{\mathrm{B}}/R. \qquad 6.11.10$$

Substituting (10) into (9), we obtain

$$T = \sum_{\mathrm{B}} \nu_{\mathrm{B}} H_{\mathrm{B}} \Big/ \sum_{\mathrm{B}} \nu_{\mathrm{B}} S_{\mathrm{B}}. \qquad 6.11.11$$

The numerator of (11) is the enthalpy of reaction ΔH and the denominator is the entropy of reaction ΔS. We now consider these separately.

For ΔH we write formally

$$\Delta H(T)=\Delta H(T')+\sum_{\mathrm{B}} \nu_{\mathrm{B}}\{H_{\mathrm{B}}(T)-H_{\mathrm{B}}(T')\}, \qquad 6.11.12$$

If for each of the substances the dependence of H on temperature has been determined calorimetrically and if in addition ΔH has been measured at any one temperature T', then by means of (12) ΔH can be calculated at any other temperature.

For ΔS we write formally

$$\Delta S(T)=\Delta S^0+\sum_{\mathrm{B}} \nu_{\mathrm{B}}\{S_{\mathrm{B}}(T)-S_{\mathrm{B}}^0\} \qquad 6.11.13$$

where the superscript ^{0} denotes the value obtained by smooth extrapolation to $T=0$. If now the dependence of H on temperature has been measured throughout the temperature range from T down to a temperature from which one can extrapolate to $T=0$, then (13) determines ΔS for all temperatures apart from the constant ΔS^0. But S^0 is the quantity discussed in detail in §§3.51–3.57. It has the value zero except for a few well understood exceptions for which its value is known to be $R \ln o$, with o a small number such as 2 or $\frac{3}{2}$. With this knowledge of ΔS^0 or in the absence of evidence to the contrary assuming $\Delta S^0=0$, formula (13) determines ΔS for all temperatures.

Using (12) and (13) together, we can solve (11) for the *transition temperature* T. Alternatively using the experimental value of T, we can use (11), (12), (13) to determine an experimental value for ΔS^0.

§6.12 *Transition of sulphur*

We shall now illustrate the formulae of the preceding section by a numerical example. As already mentioned it is difficult to find an example of an equilibrium temperature for a reaction between solid phases except in the simplest case of an allotropic change. We accordingly choose as our example

$$0=\text{monoclinic sulphur}-\text{rhombic sulphur} \qquad 6.12.1$$

and we shall use the subscripts $_{\mathrm{R}}$ and $_{\mathrm{M}}$ for the rhombic and monoclinic forms respectively. The transition temperature is

$$T=368.6\ \mathrm{K} \qquad \text{(transition).} \qquad 6.12.2$$

The enthalpy of transition at this temperature is given by

$$\Delta H/R=(H_{\mathrm{M}}-H_{\mathrm{R}})/R=(47.5\pm 5)\ \mathrm{K} \qquad (T=368.6\ \mathrm{K}). \qquad 6.12.3$$

Consequently the entropy of transition at this temperature is

$$\Delta S/R = (S_{\mathrm{M}} - S_{\mathrm{R}})/R = 47.5/368.6 = 0.12 \pm 0.01 \qquad (T = 368.6\ \mathrm{K}). \tag{6.12.4}$$

According to calorimetric measurements* on the two forms from 15 K to the transition temperature

$$\{S_{\mathrm{R}}(368.6\ \mathrm{K}) - S_{\mathrm{R}}(15\ \mathrm{K})\}/R = 4.38 \pm 0.03 \tag{6.12.5}$$

$$\{S_{\mathrm{M}}(368.6\ \mathrm{K}) - S_{\mathrm{M}}(15\ \mathrm{K})\}/R = 4.49 \pm 0.04. \tag{6.12.6}$$

Combining (4), (5), and (6) we obtain

$$\begin{aligned}\{S_{\mathrm{M}}(15\ \mathrm{K}) - S_{\mathrm{R}}(15\ \mathrm{K})\}/R &= 0.12 - 4.49 + 4.38 \\ &= 0.01 \pm 0.05.\end{aligned} \tag{6.12.7}$$

We conclude that well within the experimental accuracy

$$S^0_{\mathrm{M}} - S^0_{\mathrm{R}} = 0. \tag{6.12.8}$$

§6.13 *Homogeneous equilibrium in solution*

We turn now to homogeneous chemical equilibrium in a liquid solution. We again start from the general equilibrium condition (6.01.11)

$$\prod (\lambda) = 1 \tag{6.13.1}$$

and use

$$\lambda = \lambda^{\ominus} m \gamma. \tag{6.13.2}$$

Substituting (2) into (1) we obtain

$$\prod (m) \prod (\gamma) = K_m \tag{6.13.3}$$

where K_m is defined by

$$K_m = \prod (1/\lambda^{\ominus}) \tag{6.13.4}$$

and so depends only on the solvent and the temperature. K_m is called the *molality equilibrium constant*. Formula (3) tells us that the equilibrium molality product is inversely proportional to the equilibrium activity coefficient product.

In the special case of an ideal dilute solution (3) reduces to

$$\prod (m) = K_m. \tag{6.13.5}$$

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* Eastman and McGavock, J. Amer. Chem. Soc. 1937 **59** 145.

§6.14 *Temperature dependence*

If we take logarithms of (6.13.4) we have

$$\ln K_m = -\sum_{\mathrm{B}} \nu_{\mathrm{B}} \ln \lambda_{\mathrm{B}}^{\ominus}. \qquad 6.14.1$$

Differentiating with respect to T and using (5.15.2) we obtain

$$\mathrm{d} \ln K_m/\mathrm{d}T = \sum_{\mathrm{B}} \nu_{\mathrm{B}} H_{\mathrm{B}}^{\infty}/RT^2 = \Delta H^{\infty}/RT^2. \qquad 6.14.2$$

where ΔH^{∞} is the *enthalpy of reaction at infinite dilution* in the given solvent.

§6.15 *Use of volume concentrations*

As mentioned in §5.28 volume concentrations are sometimes used instead of molalities but the practice is not recommended. In place of (6.13.3) one then obtains

$$\prod (c) \prod (y) = K_c \qquad 6.15.1$$

where c denotes volume concentration and y denotes a new kind of activity coefficient. We shall not go into details, but will only point out that the temperature dependence of K_c is given by*

$$\partial \ln K_c/\partial T = \Delta H^{\infty}/RT^2 - \alpha \sum_{\mathrm{B}} \nu_{\mathrm{B}} \qquad 6.15.2$$

where α denotes the thermal expansivity of the solvent. Spurious formulae for $\partial \ln K_c/\partial T$ obtained by false analogy with gaseous equilibria have sometimes been quoted, both in the past and recently†.

§6.16 *Heterogeneous equilibria involving solutions*

We might also discuss equilibria involving solutions and vapour phases, or solutions and solids, or even solutions, solids, and vapour phases, but this is unnecessary because any equilibrium however complicated can be regarded as a superposition of a homogeneous equilibrium in a single phase, liquid or gaseous, and distribution equilibria of individual species between pairs of phases. Both these elementary types of equilibrium have been discussed in sufficient detail.

§6.17 *Transitions of second order*

This is perhaps the most convenient place to describe a phenomenon called

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* Guggenheim, Trans. Faraday Soc. 1937 **33** 607.

† E.g. Clarke and Glew, Trans. Faraday Soc. 1966 **62** 547.

a *transition of the second order*. It is quite different from anything we have yet met, having some of the characteristics of phase changes and some of the characteristics of critical phenomena. We shall first show by a particular example how a transition of the second order arises from certain assumed properties of the thermodynamic functions. We shall then discuss briefly how and when such transitions occur.

As a preliminary step to our discussion, we shall consider the thermodynamic properties of the equilibrium between two isomers under the simplest conceivable conditions. Thus we consider the isomeric change

$$\mathrm{A} \rightarrow \mathrm{B} \qquad 6.17.1$$

occurring in a mixture of A and B in the absence of any other species. We further assume that the mixture is ideal. Finally we assume that the proper enthalpy of reaction has a value w independent of the temperature; in other words we assume that A and B have equal heat capacities. If then x denotes the mole fraction of B the proper Gibbs function G_{m} has the form

$$G_{\mathrm{m}} = G_{\mathrm{m}}^{\ominus}(T) + xw + RT\{(1-x)\ln(1-x) + x\ln x\} \qquad 6.17.2$$

where w is a constant and $G_{\mathrm{m}}^{\ominus}(T)$ depends only on the temperature. From (2) we deduce

$$H_{\mathrm{m}} = G_{\mathrm{m}}^{\ominus} - T\mathrm{d}G_{\mathrm{m}}^{\ominus}/\mathrm{d}T + xw \qquad 6.17.3$$

from which we verify that the proper enthalpy of reaction is w. We also deduce

$$S_{\mathrm{m}} = -\mathrm{d}G_{\mathrm{m}}^{\ominus}/\mathrm{d}T - R\{(1-x)\ln(1-x) + x\ln x\} \qquad 6.17.4$$

showing that the proper entropy of mixing has its ideal value

$$-R\{(1-x)\ln(1-x) + x\ln x\}. \qquad 6.17.5$$

The equilibrium value of x is obtained by minimizing G_{m}. We find

$$\partial G_{\mathrm{m}}/\partial x = w + RT\ln\{x/(1-x)\} = 0 \qquad 6.17.6$$

so that

$$x/(1-x) = \exp(-w/RT). \qquad 6.17.7$$

Formula (7) is, of course, the simplest possible example of the equilibrium law. Before we dismiss this extremely simple system, there remains one important point to be investigated, namely the verification that (6) and (7) do correspond to a minimum of G_{m}, not to a maximum. We have

$$\partial^2 G_{\mathrm{m}}/\partial x^2 = RT\{1/x + 1/(1-x)\} > 0 \qquad 6.17.8$$

thus verifying that we have found a minimum, not a maximum.

Let us now arbitrarily introduce a modification into the form of G_{m} assumed in (2), without at this stage enquiring into the physical significance of the change. We replace the term wx by $wx(1-x)$. We then have

$$G_{\mathrm{m}}=G_{\mathrm{m}}^{\ominus}(T)+x(1-x)w+RT\{(1-x)\ln(1-x)+x\ln x\} \qquad 6.17.9$$

$$H_{\mathrm{m}}=G_{\mathrm{m}}^{\ominus}-T\,\mathrm{d}G_{\mathrm{m}}^{\ominus}/\mathrm{d}T+x(1-x)w \qquad 6.17.10$$

$$S_{\mathrm{m}}=-\mathrm{d}G_{\mathrm{m}}^{\ominus}/\mathrm{d}T-R\{(1-x)\ln(1-x)+x\ln x\} \qquad 6.17.11$$

from which we observe that the enthalpy is affected by the modification, but the entropy is not.

We now seek the equilibrium value of x by minimizing G_{m}. We find

$$\partial G_{\mathrm{m}}/\partial x=-(2x-1)w+\ln\{x/(1-x)\}=0 \qquad 6.17.12$$

so that

$$x/(1-x)=\exp\{(2x-1)w/RT\}. \qquad 6.17.13$$

One solution of (13) is obviously $x=\frac{1}{2}$, but this is not always the only solution. Nor is this solution necessarily a minimum rather than a maximum of G_{m}. We must investigate these points and shall do so in the first place graphically. Figure 6.1 shows $(G_{\mathrm{m}}-G_{\mathrm{m}}^{\ominus})/RT$ plotted against $2x-1$ for various values of $\frac{1}{2}w/RT$. Owing to the complete symmetry between x and $1-x$, we can without loss of generality assume that $x>1-x$.

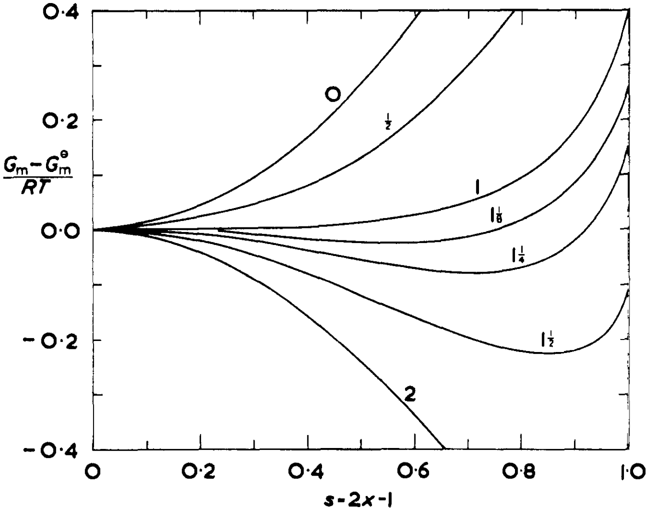

Fig. 6.1. Dependence of G_{m} on x for various values of $\frac{1}{2}w/RT$. The numbers attached to the curves are values of $\frac{1}{2}w/RT$ or T_{λ}/T

We see that if $w>0$ then at high temperatures, that is at small values of w/RT, the root $x=\frac{1}{2}$ is the only root and it corresponds to a minimum of G_m. At low enough temperatures, that is at large values of w/RT, there is another root $\frac{1}{2}\leqq x\leqq 1$ and this root corresponds to a minimum of G_m while the root $x=\frac{1}{2}$ now corresponds to a maximum. Thus there exists a temperature T_λ such that at temperatures below T_λ the equilibrium value of x is greater than $\frac{1}{2}$ and decreases as the temperature increases; the equilibrium value of x becomes $\frac{1}{2}$ at the temperature T_λ and remains $\frac{1}{2}$ at all high temperatures. The change occurring at the temperature T_λ is called a *transition of the second order* and the temperature T_λ is called a *lambda point* for a reason which will be explained later.

It is clear from figure 6.1 that T_λ is the temperature at which the two roots of (13) become equal, the root at $x=\frac{1}{2}$ changing from a minimum to a maximum. Thus there is a point of horizontal inflexion at $x=\frac{1}{2}$. We have then

$$\partial^2 G_m/\partial x^2=-2w/RT_\lambda+1/x(1-x)=0 \qquad (x=\tfrac{1}{2}) \qquad 6.17.14$$

whence

$$w/RT_\lambda=2. \qquad 6.17.15$$

It is clear from figure 6.1 that for negative values of w the minimum is always at $x=\frac{1}{2}$ and there can be no lambda point.

§6.18 *Cooperative systems*

Before proceeding to a more detailed examination of transitions of the second order, we shall explain in very general terms how they may arise. As a preliminary step, let us determine the enthalpy of change in the process (6.17.1). For the enthalpy H of the whole sytem, we have according to (6.17.10) changing to the variables n_A, n_B

$$H=(n_A+n_B)H^\ominus+n_A n_B w/(n_A+n_B) \qquad 6.18.1$$

where $H^\ominus$ is independent of n_A, n_B. Differentiating with respect to n_A, n_B in turn we obtain for the partial enthalpies

$$H_A=H^\ominus+n_B^2 w/(n_A+n_B)^2=H^\ominus+x^2 w \qquad 6.18.2$$

$$H_B=H^\ominus+n_A^2 w/(n_A+n_B)^2=H^\ominus+(1-x)^2 w \qquad 6.18.3$$

so that the proper *enthalpy of change* from A to B is

$$H_B-H_A=(1-2x)w. \qquad 6.18.4$$

Since we are considering a condensed phase, (4) is effectively equivalent to

$$U_B - U_A = (1-2x)w. \qquad 6.18.5$$

The outstanding characteristic of (5) is that the energy required to convert a molecule A into a molecule B depends in a marked degree on what fraction of all the molecules is present in each form. Such a characteristic would not be expected when the process

$$A \rightarrow B \qquad 6.18.6$$

represents a chemical change of one isomer to another, nor in such a case do we find a lambda point. It is however not difficult to mention other interpretations of (6) which might reasonably be expected to have the characteristic just mentioned. Suppose for example we consider a regular array of polar molecules or atoms in a lattice. Suppose further that each moleule or atom can point in either of two opposite directions. Suppose finally that we denote the molecules by A or B according to the direction in which they point. Then it is easily understandable that the energy required to turn round a molecule or atom may depend markedly on how many other molecules or atoms are pointing in either direction. This behaviour is typical of systems called *cooperative*. The significance of the name should be clear from this and the following examples.

Another more complicated, but possibly more important, interpretation of (6) is for A to represent a state of molecular libration and B a state of molecular rotation.

Another example occurring in certain alloys is the following. Suppose we have an alloy of the composition ZnCu containing N atoms of Zn and N atoms of Cu arranged on a regular lattice of $2N$ lattice points. We can picture two extreme arrangements of the two kinds of atoms on the lattice, one completely ordered, the other completely random. In the completely ordered arrangement every alternate lattice point A is occupied by a Zn atom and the remaining lattice points B are occupied by Cu atoms. In the opposite extreme arrangement every lattice point A or B is occupied by either Zn or Cu atoms arranged at complete random. We can moreover consider intermediate arrangements such that a fraction x of the Zn atoms occupy A lattice points and the fraction $1-x$ of Zn atoms occupy B lattice points. The remaining lattice points are of course occupied by the Cu atoms. We can then without loss of generality take $x \geqq \frac{1}{2}$. In such a system the average energy required to move a Zn atom from an A point to a B point will depend markedly on how many A points are already occupied by Zn atoms. It is therefore at least conceivable that such a system might have a lambda point.

As a matter of fact the alloy having the composition ZnCu does have a lambda point and the thermodynamic properties of this system can be at least semi-quantitatively represented by a Gibbs function of the form (6.17.9). This form was first suggested by Gorsky* and later independently derived by approximate statistical considerations by Bragg and Williams[†]. It is outside the scope of this book to consider this aspect of the phenomenon and we shall accordingly confine ourselves to a purely phenomenological thermodynamic investigation of some of the general properties of lambda points, among others the property leading to the name.

§6.19 *Alternative notation*

The notation which we have used to introduce the subject of *transitions of the second order* seems natural. It is not however the notation most used. For the sake of completeness we describe briefly the alternative notation.

A quantity s called the *degree of order* is defined by[†]

$$s = 2x - 1 \qquad 6.19.1$$

or

$$x = \tfrac{1}{2}(1+s). \qquad 6.19.2$$

In this notation formula (6.17.9) becomes

$$G_{\mathrm{m}} = G_{\mathrm{m}}^{\ominus} + \tfrac{1}{4}(1-s^2)w + RT\{\tfrac{1}{2}(1+s)\ln(1+s) + \tfrac{1}{2}(1-s)\ln(1-s) - \ln 2\}. \qquad 6.19.3$$

The equilibrium value of s is determined according to (6.17.12) by

$$\ln\{(1+s)/(1-s)\} = sw/RT \qquad 6.19.4$$

which is equivalent to

$$\tanh(ws/2RT) = s. \qquad 6.19.5$$

Using (6.17.15) we can transform (5) to

$$T_{\lambda}/T = (\tanh^{-1}s)/s. \qquad 6.19.6$$

These formulae, of course, contain nothing which is not already contained in the formulae of §6.17. It is merely a historical accident that pioneer workers in this field used the variable s instead of x.

§6.20 *Lambda point*

We have seen how a Gibbs function of the form (6.17.9) leads without any

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* Gorsky, Z. Phys. 1928 **50** 64.

[†] Bragg and Williams, Proc. Roy. Soc. A 1934 **145** 699.

further assumption to the occurrence of a *transition of the second order* and we have explained how this type of behaviour can occur in a *cooperative system*. We do not assert that a Gibbs function of approximately this form is the origin of all transitions of the second order. Still less do we assert that a Gibbs function of this form accounts accurately for any transition of the second order. We merely assert that the form (6.17.9) of the Gibbs function is one possible form which leads to the occurrence of a lambda point having certain general characteristics which we shall describe. We shall continue to make use of the particular forms of thermodynamic functions described in §6.17 merely for illustrative purposes.

From figure 6.1, or more accurately by calculation from (6.17.13), we can determine the equilibrium value of x as a function of T. The result is given in figure 6.2, where $s=2x-1$ is plotted against T/T_λ. We notice that at temperatures immediately below T_λ the equilibrium value of s changes rapidly with temperature and at temperatures below $\frac{1}{2}T_\lambda$ this equilibrium value differs hardly appreciably from unity. There is then a rapid change of the equilibrium value of s in the temperature range between T_λ and $\frac{1}{2}T_\lambda$. Associated with this change in s there is a rapid change in the part of the proper energy or enthalpy which depends on s namely the term

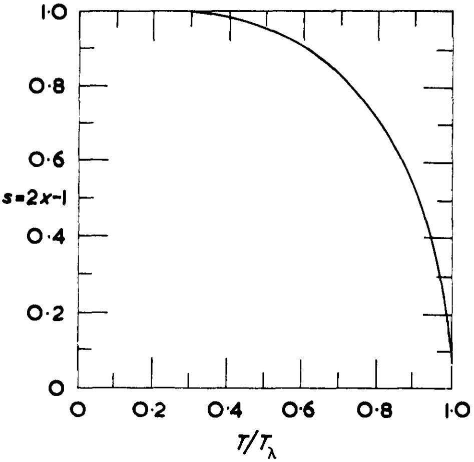

Fig. 6.2. Dependence of equilibrium value of degree of order on temperature

$$x(1-x)w=\tfrac{1}{4}(1-s^2)w. \qquad 6.20.1$$

This is shown in figure 6.3. The term (1) occurs in the energy additional to other terms due to the translational and internal degrees of freedom of the molecules. Thus as the temperature is decreased through the lambda point

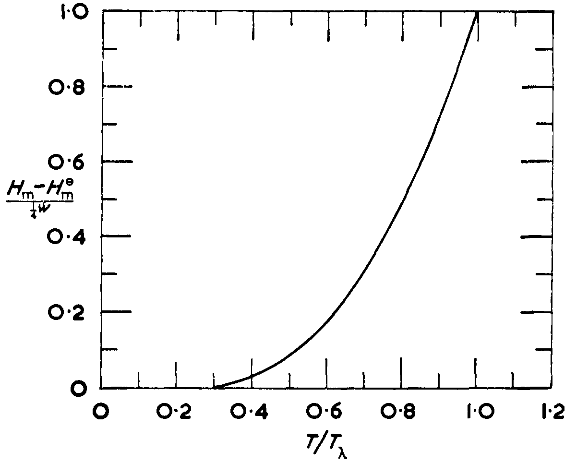

Fig. 6.3. Temperature dependence of enthalpy due to variation in degree of order

there is a sudden change in the temperature coefficient of the enthalpy, or in other words a discontinuity in the heat capacity C. This is shown in figure 6.4. The shape of the curve recalls a Greek capital Λ whence the name *lambda point* suggested by Ehrenfest.*

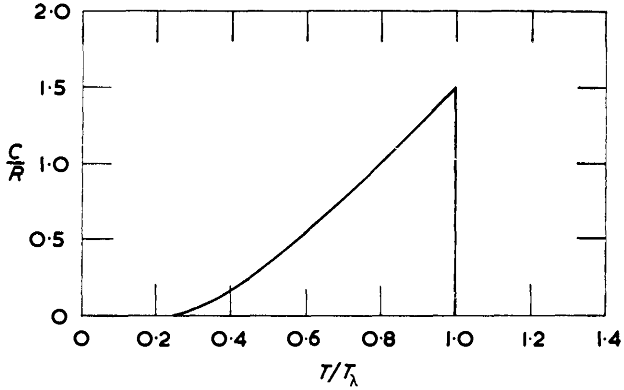

Fig. 6.4. Contribution to heat capacity of variation in degree of order

For the particular model considered in detail, we observe that in the immediate neighbourhood below the lambda temperature

$$\partial H/\partial s = 0 \tag{6.20.2}$$

$$\partial S/\partial s = 0 \tag{6.20.3}$$

$$ds/dT = \infty \tag{6.20.4}$$

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* Keesom, Helium, Elsevier, 1942 p. 216.

in such a manner that

$$(\partial H/\partial s)(\mathrm{d}s/\mathrm{d}T) \text{ is finite} \tag{6.20.5}$$

$$(\partial S/\partial s)(\mathrm{d}s/\mathrm{d}T) \text{ is finite.} \tag{6.20.6}$$

The properties (5) and (6) are independent of the choice of s. On the other hand the relations (2), (3), (4) depend on the definition of s. For example if we replace s by $\sigma = s^2$, then

$$\partial H/\partial\sigma \text{ is finite} \tag{6.20.7}$$

$$\partial S/\partial\sigma \text{ is finite.} \tag{6.20.8}$$

We may then describe a transition of the second order as a discontinuity in C, with continuity of H, S, G, at a certain temperature T_λ called the *lambda point.*

The lambda point known longest is the one discovered by Curie and therefore called the *Curie point,* below which a substance such as iron has permanent magnetization and above which it has not. The Curie point will be referred to again in chapter 11.

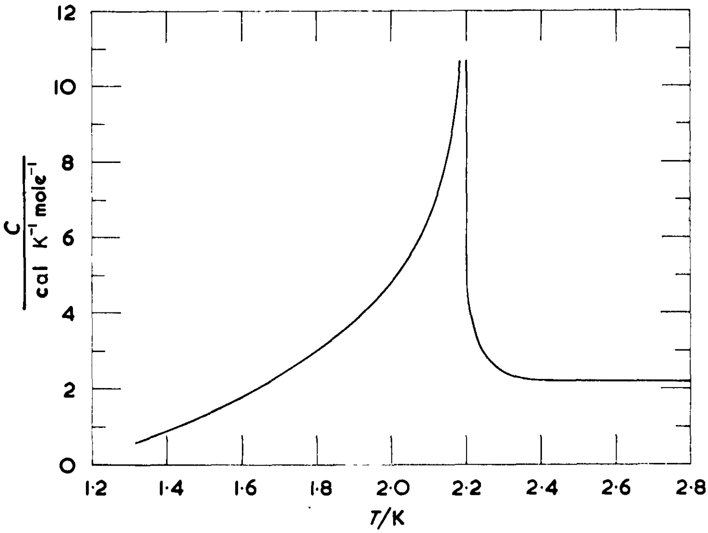

Fig. 6.5. Heat capacity of liquid helium near lambda point

Probably the most interesting, most studied, but perhaps least understood lambda point is that of helium at 2.2 K. The experimental data* for C plotted against T are shown in figure 6.5.

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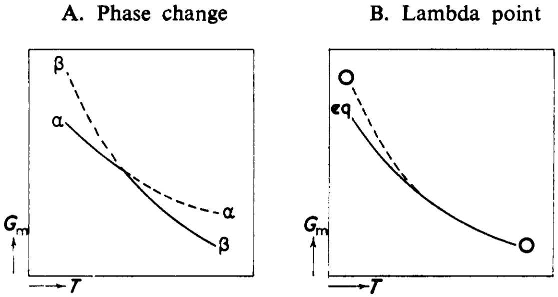
* Keesom, Helium, Elsevier, 1942 p. 215.

Many other lambda points are known to occur in crystals and are usually associated with a sudden change in the extent to which the molecules in the crystal can rotate freely. Few however, if any, have been studied in such detail as to be completely understood.

§6.21 *Comparison with phase change and critical point*

Since a substance has measurably different properties above and below the lambda point, there is a temptation to regard a *transition of the second order* as a kind of *phase change.* The expression *phase change of the second order* has been used, but as it has in the past led to considerable confusion it is better avoided.*



A. Phase change

B. Lambda point

Fig. 6.6. Contrast between phase change and lambda point

The contrast between a lambda point and a phase change may be made clear by a plot of the proper Gibbs function against the temperature. This is shown in figure 6.6. Diagram A depicts a phase change. The curves of the two distinct phases α and β cut at the transition point, the dotted portions of the curves representing metastable states. Diagram B depicts a transition of the second order. The curve marked O represents the Gibbs function of a hypothetical phase with $s=0$, which is usually associated with complete randomness. The curve marked eq represents the Gibbs function of a phase in which at each temperature s has its equilibrium value. Below the lambda point the dotted curve marked O lies above the curve marked eq and consequently the former represents metastable states.

At the lambda point the two curves touch. We might ask what happens to the eq curve above the lambda point. If we extend the eq curve by the simplest analytical formula, ignoring physics, the curve would continue below the O curve, thus suggesting that it represents states more stable than the O curve. On further study we should however find that this hypothetical

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* Guggenheim, Proc. Acad. Sci. Amst. 1934 37 3.

curve corresponds to negative values of s^2 and has therefore no physical meaning. It is therefore safer and more profitable to forget about such a curve.

On the other hand a comparison between a lambda point and a critical point, if not carried too far, is less dangerous. At temperatures below the lambda point there is a stable phase with a value of s determined by the temperature and there can also be a metastable phase with $s=0$; the latter can in fact sometimes be realized in practice by sudden chilling from a temperature above the lambda point. The difference between these two phases, measured by the values of s^2 gradually decreases as the temperature is raised and vanishes at the lambda point when the two phases become identical. This recalls the behaviour of liquid and vapour phases at the critical point, but here the resemblance ends.

§6.22 *Dependence of lambda point on pressure*

Up to this point we have considered how a transition of the second order occurs at a certain temperature, disregarding the pressure. This is in practice justifiable for most such transitions, but in principle there can be a dependence on the pressure. In practice the only known example where pressure changes are likely to be important is that of liquid helium. Let us then consider how the lambda point is affected when the pressure is changed.

In the particular model represented by (6.17.9) the dependence on pressure would result from the energy parameter w being a function of the pressure. We shall however not assume this model nor any other detailed model, but shall rather derive formulae of complete generality.

Regarding G as a function of s, as well as of T, P we have

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P + (\partial G/\partial s)\mathrm{d}s \qquad 6.22.1$$

and differentiating throughout with respect to s

$$\mathrm{d}(\partial G/\partial s) = -(\partial S/\partial s)\mathrm{d}T + (\partial V/\partial s)\mathrm{d}P + (\partial^2 G/\partial s^2)\mathrm{d}s. \qquad 6.22.2$$

Now the equilibrium value of s at each temperature is determined by

$$\partial G/\partial s = 0 \qquad \text{(equilibrium)} \qquad 6.22.3$$

and in particular at the lambda point

$$s = 0 \qquad \text{(lambda point).} \qquad 6.22.4$$

If then we follow the lambda point at varying pressure we have (3) and owing to (4) we have

$$\mathrm{d}s=0 \qquad \text{(lambda point).} \tag{6.22.5}$$

Substituting (3) and (5) into (2) we obtain

$$-(\partial S/\partial s)\mathrm{d}T+(\partial V/\partial s)\mathrm{d}P=0 \qquad \text{(lambda point)} \tag{6.22.6}$$

or

$$\frac{\mathrm{d}T_\lambda}{\mathrm{d}P}=\frac{(\partial V/\partial s)_{s=0}}{(\partial S/\partial s)_{s=0}}. \tag{6.22.7}$$

Formula (7) describes in the most general way how the temperature of the lambda point depends on the pressure. The right side of (7) can however usefully be transformed into alternative forms more directly related to experimental quantities.

We accordingly multiply numerator and denominator of (7) by $\mathrm{d}s/\mathrm{d}T$, where s here denotes the equilibrium value. We obtain

$$\frac{\mathrm{d}T_\lambda}{\mathrm{d}P}=\frac{\partial V}{\partial s}\frac{\mathrm{d}s}{\mathrm{d}T}\Bigg/\frac{\partial S}{\partial s}\frac{\mathrm{d}s}{\mathrm{d}T} \tag{6.22.8}$$

where every quantity on the right side is given its equilibrium value at or immediately below T_λ. We shall now examine the physical significance of the numerator and denominator on the right of (8).

Let us use the superscripts $^-$ and $^+$ to denote the value of quantities immediately below and immediately above the temperature T_λ. Then we have

$$G^-=G^+ \tag{6.22.9}$$

$$H^-=H^+ \tag{6.22.10}$$

$$S^-=S^+ \tag{6.22.11}$$

$$C^-=C^++T_\lambda(\partial S/\partial s)(\mathrm{d}s/\mathrm{d}T) \tag{6.22.12}$$

so that the denominator on the right of (8) is $(C^--C^+)/T_\lambda$.

Similarly if α denotes coefficient of thermal expansion

$$V^-=V^+=V_\lambda \tag{6.22.13}$$

$$\alpha^-V_\lambda=\alpha^+V_\lambda+(\partial V/\partial s)(\mathrm{d}s/\mathrm{d}T) \tag{6.22.14}$$

so that the numerator in (8) is $(\alpha^--\alpha^+)V_\lambda$. Hence substituting (12) and (14) into (8) we obtain

$$\mathrm{d}T_\lambda/\mathrm{d}P=(\alpha^--\alpha^+)V_\lambda T_\lambda/(C^--C^+). \tag{6.22.15}$$

This formula shows how the effect of pressure on the lambda point is related to the discontinuities in C and in α.

Returning to (7), instead of multiplying numerator and denominator by ds/dT, we multiply by ds/dP, obtaining

$$\frac{\mathrm{d}T_\lambda}{\mathrm{d}P} = \frac{\partial V}{\partial s}\frac{\mathrm{d}s}{\mathrm{d}P}\bigg/\frac{\partial S}{\partial s}\frac{\mathrm{d}s}{\mathrm{d}P}. \tag{6.22.16}$$

But if κ_T denotes isothermal compressibility, we have

$$\kappa_T^- V_\lambda = \kappa_T^+ V_\lambda - (\partial V/\partial s)(\mathrm{d}s/\mathrm{d}P). \tag{6.22.17}$$

Similarly

$$\left(\frac{\partial S}{\partial P}\right)^- = \left(\frac{\partial S}{\partial P}\right)^+ + \frac{\partial S}{\partial s}\frac{\mathrm{d}s}{\mathrm{d}P} \tag{6.22.18}$$

and so using Maxwell's relation (1.47.4) we have

$$\alpha^- V_\lambda = \alpha^+ V_\lambda - (\partial S/\partial s)(\mathrm{d}s/\mathrm{d}P). \tag{6.22.19}$$

Substituting (17) and (19) into (16) we obtain

$$\mathrm{d}T_\lambda/\mathrm{d}P = (\kappa_T^- - \kappa_T^+)/(\alpha^- - \alpha^+). \tag{6.22.20}$$

This formula relates the dependence of the lambda point on the pressure to the discontinuities in α and κ_T.

Formulae (15) and (20) are due to Ehrenfest.*

§6.23 *Transitions of higher order*

In an ordinary *phase change*, which we may call a *transition of the first order*, we have

$$\left.\begin{array}{ll} G & \text{continuous} \\ S = -\partial G/\partial T & \text{discontinuous} \end{array}\right\} \text{1st order transitions.}$$

In the *transitions of the second order*, which we have been discussing, we have

$$\left.\begin{array}{ll} G,\ \partial G/\partial T & \text{continuous} \\ C = -T\partial^2 G/\partial T^2 & \text{discontinuous} \end{array}\right\} \text{2nd order transitions.}$$

In a like manner we can define a *transition of the third order* by

$$\left.\begin{array}{ll} G,\ \partial G/\partial T,\ \partial^2 G/\partial T^2 & \text{continuous} \\ \partial^3 G/\partial T^3 & \text{discontinuous} \end{array}\right\} \text{3rd order transitions.}$$

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* Ehrenfest, Proc. Acad. Sci. Amst. 1933 36 153.

It is possible that transitions of the third order exist. It is further possible to extend the above definitions to transitions of still higher order. We shall however not pursue this matter any further.

§6.24 *Components and degrees of freedom*

Since the equilibrium condition for the chemical change

$$0=\sum_{\mathrm{B}} \nu_{\mathrm{B}}\mathrm{B} \qquad 6.24.1$$

is given by (6.01.7)

$$\sum_{\mathrm{B}} \nu_{\mathrm{B}}\mu_{\mathrm{B}}=0 \qquad 6.24.2$$

all variations of temperature, pressure, and composition consistent with chemical equilibrium must satisfy

$$\sum_{\mathrm{B}} \nu_{\mathrm{B}}\mathrm{d}\mu_{\mathrm{B}}=0. \qquad 6.24.3$$

This is a relation between the chemical potentials additional to and independent of the Gibbs–Duhem relations. The existence of this relation reduces by one the number of degrees of freedom of the system.

Let us consider a particular example, namely a gaseous mixture of N_2, H_2, and NH_3, regarded as perfect. This single-phase system can be described by T, P, x_{N_2}, x_{H_2}, x_{NH_3} subject to the identity

$$x_{N_2}+x_{H_2}+x_{NH_3}=1 \qquad 6.24.4$$

or alternatively by T, P, μ_{N_2}, μ_{H_2}, μ_{NH_3} subject to the Gibbs–Duhem relation

$$x_{N_2}\mathrm{d}\mu_{N_2}+x_{H_2}\mathrm{d}\mu_{H_2}+x_{NH_3}\mathrm{d}\mu_{NH_3}=0. \qquad 6.24.5$$

Hence in the absence of chemical reaction between the three components the system has four degrees of freedom. If however, for example by introducing a catalyst, we enable the process

$$N_2+3H_2\rightleftharpoons 2NH_3 \qquad 6.24.6$$

to attain equilibrium, then there is the further restriction

$$\mu_{N_2}+3\mu_{H_2}=2\mu_{NH_3} \qquad 6.24.7$$

which reduces the number of degrees of freedom from four to three. This situation is sometimes described by saying that of the three species N_2, H_2, and NH_3 there are only two *independent components*. Whether or not this terminology is adopted the number of degrees of freedom is certainly three.

As a second example consider the system consisting of PCl_3, Cl_2, and PCl_5. There are three chemical species but owing to the equilibrium condition for the reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad 6.24.8$$

there are only two independent components. For the gaseous phase alone the situation is similar to that in the system N_2, H_2, and NH_3. There are two independent components in one phase and so three degrees of freedom. If we consider the system consisting of the solid phase PCl_5 together with the gaseous phase we have two independent components in two phases and so two degrees of freedom. This means that there are two independent variables which we shall take to be the temperature T and the stoichiometric ratio r of Cl to P in the gas phase. The temperature determines the equilibrium constant K for the process

$$PCl_5(s) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad 6.24.9$$

and the fugacities are then determined by the simultaneous equations

$$p_{PCl_3} p_{Cl_2} = K \qquad 6.24.10$$

$$(3p_{PCl_3} + 2p_{Cl_2})/p_{PCl_3} = r. \qquad 6.24.11$$

In the particular case $r=5$ the stoichiometric composition of the gas phase is the same as that of the solid phase PCl_5. In this case some authors go so far as to describe the system as of one component PCl_5. This attitude has nothing to recommend it. We have seen that the system as initially described has two degrees of freedom. These two degrees of freedom are of course reduced to one by specifying the value of r but the value $r=5$ has no unique thermodynamic feature. The statement that the ratio of Cl to P in the gas phase is equal to its ratio in the solid phase is no different in kind from the statement that the ratio in the gas phase is one half, or double, the ratio in the solid phase. The distinction between $r=5$ and other values of r is artificial and pointless. Furthermore it can lead to confusion. Suppose we are interested in the surface phase between solid and gas. Then although the ratio of Cl to P may be 5 in both gas phase and solid there is no reason to expect the ratio to be 5 in the surface phase. In other words there may well be preferential adsorption of either PCl_3 or Cl_2 and this can not be described in terms of the single component PCl_5. Again suppose there is a gravitational field. Then, as we shall see in chapter 9, the proportion of PCl_3 to Cl_2 will vary from layer to layer and can have the value unity at one height only. It is then essential to treat the system as of two components even though the overall stoichiometric composition may be that of PCl_5.

Now consider a system in which several chemical changes can take place. Some such changes may be expressible as linear combinations of others, but there will always be a definite number of chemical changes which are linearly independent. Consider for example a system consisting of solid graphite and a perfect gaseous mixture O_2, CO, CO_2. Then of the chemical changes

$$C+\tfrac{1}{2}O_2 \rightarrow CO \tag{6.24.12}$$

$$C+O_2 \rightarrow CO_2 \tag{6.24.13}$$

$$CO+\tfrac{1}{2}O_2 \rightarrow CO_2 \tag{6.24.14}$$

$$C+CO_2 \rightarrow 2CO \tag{6.24.15}$$

the third is obtained by subtracting the first from the second, while the fourth is obtained by subtracting the third from the first. Thus only two of these changes are independent. By a comparison of (1) and (2) it is clear that independent chemical processes have independent equilibrium conditions, whereas linearly related chemical processes have linearly related equilibrium conditions. Hence each linearly independent chemical equilibrium corresponds to a restrictive relation between the chemical potentials leading to a decrease by unity in the number of degrees of freedom. For example in the two-phase system consisting of solid graphite and a gaseous mixture of O_2, CO, CO_2 the effect of the two independent chemical equilibria is to reduce the number of degrees of freedom from four to two; thus the state of the system is completely determined by the temperature and the pressure. Incidentally in this particular system at equilibrium the amount of free O_2 is so small as to be undetectable. The system may therefore be more simply described as a two-phase system containing the three species C, CO, and CO_2 between which there is a single chemical reaction

$$C+CO_2 \rightarrow 2CO. \tag{6.24.16}$$

The equilibrium condition for this process reduces the number of degrees of freedom from three to two. Whichever way we consider the system we find that the number of degrees of freedom is two. Whether we regard the system as consisting of four components with two independent chemical processes, of three components with one independent chemical process, or of two independent components is a mere difference of terminology without practical importance.