CHAPTER 1

FUNDAMENTAL PRINCIPLES

§1.01 *Scope of thermodynamics*

The most important conception in thermodynamics is temperature. The essential properties of temperature will be described below. Anticipating this we may define thermodynamics as that part of physics concerned with the dependence on temperature of any equilibrium property. This definition may be illustrated by a simple example. Consider the distribution of two immiscible liquids such as mercury and water in a gravitational field. The equilibrium distribution is that in which the heavier liquid, mercury, occupies the part of accessible space where the gravitational potential is lowest and the lighter liquid, water, occupies the part of the remaining accessible space where the gravitational potential is lowest. This equilibrium distribution, if we neglect the effect of thermal expansion, is independent of temperature. Consequently the problem does not involve thermodynamics, but only hydrostatics. Now consider by contrast the distribution in a gravitational field of two completely miscible fluids such as bromine and carbon disulphide. The relative proportions of the two substances will vary from place to place, the proportion of the heavier liquid, bromine, being greatest at the lowest gravitational potential and conversely. The precise relation between the composition and the gravitational potential depends on the temperature, assumed uniform, of the mixture. Clearly this is a problem in thermodynamics, not merely hydrostatics.

We shall now mention a few other typical examples to show that thermodynamics has a bearing on most branches of physics, including elasticity, hydrodynamics, electrostatics, and electrodynamics. In the relation, known as Hooke's law, of proportionality between tension and extension the coefficient of proportionality will in general be temperature dependent. In so far as its variation with temperature is relevant thermodynamics is involved. To study the temperature dependence of the compressibility of a fluid, that of the permittivity of a dielectric, that of the permeability of a paramagnetic material, that of the electromotive force of a cell, and in fact the temperature dependence of any equilibrium property, thermodynamics is needed,

The name 'thermodynamics' is too firmly established to be changed, but a better name is 'thermophysics' containing as branches 'thermodynamics' or 'thermomechanics', 'thermoelasticity', 'thermoelectrostatics', 'thermomagnetics', 'thermochemics', and so on.

§1.02 *Thermodynamic state. Phases*

The simplest example of a system to which thermodynamics can be applied is a single homogeneous substance. In this simplest case a complete description of its thermodynamic state requires a specification of its content, i.e. amount of each chemical substance contained, and further a specification of two other quantities such as for example volume and viscosity, or density and pressure. If all the physical properties of the system in which we are interested were independent of whether the system is hot or cold, then in order to describe its state it would be sufficient to specify, apart from the amount of each chemical substance contained, only one quantity, such as volume. Usually some, if not all, of the properties of interest do depend on whether the body is hot or cold and the specification of one extra independent quantity fixes the degree of hotness or coldness. Thus this simple *thermo-hydrodynamic* system has one more degree of freedom than the corresponding *hydrodynamic* system.

If the system is not homogeneous, then in order to describe its thermodynamic state we have to consider it as composed of a number, small or large, of homogeneous parts called *phases* each of which is described by specifying its content and a sufficient number of other properties; the sufficient number for each *thermo-physical* phase is always one more than in the corresponding hypothetical *physical* system with all its properties of interest independent of whether it is hot or cold.

In some cases the complete description of the thermodynamic state of a system may require it to be regarded as composed of an infinite number of infinitesimal phases. If the physical properties vary continuously over macroscopic parts of the system, this procedure offers no difficulty. An example is a high column of gas in a gravitational field. If on the other hand there are infinitely many discontinuities over finite regions, it may be difficult if not impossible to give a complete description of the thermodynamic state. An example is a gas flowing turbulently through an orifice.

In considering the properties of interfaces, we shall have to include phases which are extremely thin in the direction normal to the interface.

To sum up, the complete description of the thermodynamic state of any system involves a description of the thermodynamic state of each of its homogeneous phases, which may be few or many or infinite in number. The description of the thermodynamic state of each phase requires the specification of one more property than the description of the physical state of an analogous hypothetical phase all of whose properties of interest are independent of whether it be hot or cold.

§1.03 *Thermodynamic process*

If on comparing the state of a thermodynamic system at two different times it is found that there is a difference in any macroscopic property of the system, then we say that between the two times of observation a *process* has taken place. If, for example, two equal quantities of gas are allowed to intermix, this will constitute a *process* from a thermodynamic point of view provided the two initially separate gases are distinguishable by any macroscopic property, even though their difference is very slight as would be the case for two isotopes. If, on the other hand, the two initially separate gases are not distinguishable by any macroscopic property, then from a thermodynamic point of view no process takes place although from a molecular point of view there is a never-ceasing intermixing.

§1.04 *Infinitesimal process*

A process taking place to such an extent that there is only an infinitesimal change in the macroscopic properties of a system is called an *infinitesimal process.*

§1.05 *Insulating walls. Adiabatic processes*

The boundary or wall separating two systems is said to be *insulating* if it has the following property. If any system in complete internal equilibrium is completely surrounded by an *insulating* wall then no change can be produced in the system by external agency except by

(a) movement of the containing wall or part of it, or

(b) long range forces, e.g. movement of electrically charged bodies.

When a system is surrounded by an insulating boundary the system is said to be *thermally insulated* and any process taking place in the system is called *adiabatic*. The name adiabatic appears to be due to Rankine*.

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* Maxwell, Theory of Heat, Longmans 1871 ed. p. 129.

§1.06 *Conducting walls. Thermal equilibrium*

The boundary or wall separating two systems is said to be *thermally conducting* if it has the following property. If any two separate systems each in complete internal equilibrium are brought together so as to be in contact through a *thermally conducting* wall then in general the two systems will be found not to be in mutual equilibrium, but will gradually adjust themselves until eventually they do reach mutual equilibrium after which there will of course be no further change. The two systems are then said to have reached a state of *thermal equilibrium.* Systems separated by a conducting boundary are said to be in *thermal contact.*

§1.07 *Zeroth law. Temperature*

We are now ready to formulate one of the important principles of thermodynamics.

If two systems are both in thermal equilibrium with a third system then they are in thermal equilibrium with each other.

This will be referred to as the *zeroth law* of thermodynamics.

Consider now a reference system in a well-defined state. Then all other systems in thermal equilibrium with it have a property in common, namely the property of being in thermal equilibrium with one another. This property is called *temperature.* In other words systems in *thermal equilibrium* are said to have the *same temperature.* Systems not in thermal equilibrium are said to have different temperatures.

§1.08 *Thermostats and thermometers*

Consider now two systems in thermal contact, one very much smaller than the other, for example a short thin metallic wire immersed in a large quantity of water. If the quantity of water is large enough (or the wire small enough), then in the process of attaining thermal equilibrium the change in the physical state of the water will be negligible compared with that of the wire. This situation is described differently according as we are primarily interested in the small system or in the large one.

If we are primarily interested in the small system, the wire, then we regard the water as a means of controlling the temperature of the wire and we refer to the water as a *temperature bath* or *thermostat.*

If on the other hand we are primarily interested in the large system, the water, we regard the wire as an instrument for recording the temperature of the water and we refer to the wire as a *thermometer.* This recording of temperature can be rendered quantitative by measuring some property of the thermometer, such as its electrical resistance, which varies with temperature.

§1.09 *Temperature scales*

The choice of thermometers is very wide especially as there is a choice both of the substance constituting the thermometer and of the property measured. Consequently there is a wide, effectively infinite, choice of temperature scales. There is however one particular scale which has outstandingly simple characteristics which can be described in a manner independent of the properties of any particular substance or class of substances. This temperature is called *thermodynamic temperature* or *absolute temperature.* It was first defined by Kelvin* and is denoted by T. It is the only scale that we shall use. It will be defined by its properties, especially its relation to entropy. The question how T can best be measured must necessarily be postponed to chapter 3.

§1.10 *Energy and heat. First law*

Leaving temperature for the moment, we must now say something about energy. The conception of energy arose first in mechanics and was extended to electrostatics and electrodynamics. When these branches of physics are idealized so as to exclude friction, viscosity, hysteresis, temperature gradients, temperature dependence of properties, and related phenomena, the fundamental property of energy can be described in two alternative ways.

I. When several systems interact in any way with one another, the whole set of systems being isolated from the rest of the universe, the sum of the energies of the several systems remains constant.

II. When a single system interacts with the rest of the universe (its surroundings) the increase of the energy of this system is equal to the work done on the system by the rest of the universe (its surroundings).

Under the idealized conditions mentioned above these two descriptions are equivalent, but when these restrictions are removed the two descriptions are no longer equivalent and we have to make a choice between them. Of the alternatives we choose I and with this choice the *energy* is denoted by U. The formulation I is then a statement of the conservation of energy.

Let us now consider in greater detail the interaction between a pair of

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* W. Thomson, Proc. Cambridge Phil. Soc. 1848 **1** 69.

systems, supposed isolated from the rest of the universe. Using superscripts $^{\mathrm{A}}$, $^{\mathrm{B}}$ to relate to the two systems we have

$$\mathrm{d}U^{\mathrm{A}}+\mathrm{d}U^{\mathrm{B}}=0 \tag{1.10.1}$$

or

$$\mathrm{d}U^{\mathrm{A}}=-\mathrm{d}U^{\mathrm{B}} \tag{1.10.2}$$

but in general this is not equal to the work w_{BA} done by B on A. In other words there can be exchange of energy between A and B of a kind other than work. Such an exchange of energy is that determined by a temperature difference and is called *heat*. If then we denote the heat flow from B to A by q_{BA}, we have the following relations

$$\mathrm{d}U^{\mathrm{A}}=w_{\mathrm{BA}}+q_{\mathrm{BA}} \tag{1.10.3}$$

$$\mathrm{d}U^{\mathrm{B}}=w_{\mathrm{AB}}+q_{\mathrm{AB}} \tag{1.10.4}$$

$$w_{\mathrm{AB}}+w_{\mathrm{BA}}=0 \tag{1.10.5}$$

$$q_{\mathrm{AB}}+q_{\mathrm{BA}}=0. \tag{1.10.6}$$

This set of relations together constitutes the *first law* of thermodynamics.

The sign of q is determined by the temperature difference between A and B, and the universal convention is to define the sign of a temperature difference in such a way that heat flows from the higher to the lower temperature.

The above analysis of the most general interaction between two systems can immediately be extended to the most general interaction between a given system and the rest of the universe. If we denote by U^{Σ} the energy of the system Σ, by q the heat flow from the surroundings to the system, and by w the work done on the system, we have

$$\mathrm{d}U^{\Sigma}=q+w. \tag{1.10.7}$$

The extension of the mechanical principle of conservation of energy to include changes in thermal energy and the flow of heat was a gradual process, the earlier formulations being less rigorous than later ones. The principle is implied in a posthumous publication of Carnot* (died 1832) and was placed on a firm experimental basis by Joule† (1840–45). More explicit statements of the principle were formulated by Helmholtz‡ (1847) and by

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[*] Carnot, Réflexions sur la puissance motrice du feu, Bachelier, Paris, 1824. Reprinted in 1912 by Hermann, Paris and in 1953 by Blanchard, Paris, together with some notes discovered after Carnot's death in 1832 and communicated to the Académie des Sciences in 1878 by Carnot's brother.

[†] Joule, Phil. Mag. 1845 **27** 205.

[‡] Helmholtz, Über die Erhaltung der Kraft, Physik. Ges. Berlin 1847.

Clausius* (1850). A completely rigorous formulation was given by Born† (1921).

§1.11 *Conversion of work to heat*

The expression *conversion of work to heat* should be used with caution if at all, since in general w and $-q$ are not numerically equal to each other. If however a system Σ is taken through a complete cycle, then since its initial and final states are identical the initial and final values of U^{Σ} are the same and so

$$\Delta U^{\Sigma}=0 \qquad w=-q \qquad \text{(complete cycle).} \tag{1.11.1}$$

We may then say that in the cycle the work w done on the system is converted into the balance of heat $-q$ given off by the system during the cycle, that is to say the excess of the heat given off over the heat absorbed in various parts of the cycle.

Again if a system Σ is kept in a steady state while work is done on it, then, since its state remains unaltered, U does not change and so

$$\Delta U^{\Sigma}=0 \qquad w=-q \qquad \text{(steady state).} \tag{1.11.2}$$

Here again we may say that in the steady state the work w done on the system is converted into the heat $-q$ given off by the system.

Except in the two special cases just mentioned, it is in general dangerous, if not meaningless, to speak of the conversion of work into heat or vice-versa. Unfortunately the expression is sometimes used incorrectly. Let us consider two simple practical examples which serve to illustrate the correct and incorrect use of the expression.

Consider as our system an ordinary *electric heater*, that is to say a resistor across which an electric potential difference E can be produced by closing a switch. Suppose that initially the resistor is in thermal equilibrium with its surroundings and the switch is open. When the switch is closed a current i flows through the resistor and the electrical work done on the resistor in an element of time $\mathrm{d}t$ is

$$w=Ei\mathrm{d}t. \tag{1.11.3}$$

In the first instant this work produces an increase in the energy U^{R} of the resistor R, so that

$$w=\mathrm{d}U^{\mathrm{R}} \qquad \text{(initially).} \tag{1.11.4}$$

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[*] Clausius, Ann. Phys. Lpz. 1850 **79** 368, 500.

[†] Born, Phys. Z. 1921 **22** 218.

But immediately the temperature of the resistor becomes higher than that of its surroundings and so there is a flow of heat $-q$ from the resistor to its surroundings. Thus in a given time

$$w = \mathrm{d}U^{\mathrm{R}} - q \qquad \text{(generally).} \qquad 1.11.5$$

As the temperature difference between the resistor and its surroundings increases, so $-q/w$ increases towards the value unity. Eventually a steady state is reached, the temperature of the resistor no longer increases, and we have

$$w = -q \qquad \mathrm{d}U^{\mathrm{R}} = 0 \qquad \text{(steady state).} \qquad 1.11.6$$

Only when this steady state has been reached, and not until then, may one correctly speak of the conversion of the work w into the heat $-q$.

Now by way of contrast consider the system consisting of the electric heater together with a fluid surrounding it, the whole being thermally insulated. The work done on the system is still given by (3). But now since the whole system Σ, consisting of resistor and fluid, is thermally insulated q is by definition zero, so that

$$w = \mathrm{d}U^{\Sigma} \qquad q = 0 \qquad \text{(thermal insulation).} \qquad 1.11.7$$

We may now say that the work w is converted into energy; to speak of its conversion to heat would be nonsense.

§1.12 *Natural and reversible processes*

We must now consider a classification of processes due to Planck*. All the independent infinitesimal processes that might conceivably take place may be divided into three types: *natural processes*, *unnatural processes*, and *reversible processes*.

Natural processes are all such as actually do occur; they proceed in a direction towards equilibrium.

An *unnatural process* is one in a direction away from equilibrium; such a process never occurs.

As a limiting case between natural and unnatural processes we have *reversible processes*, which consist of the passage in either direction through a continuous series of equilibrium states. Reversible processes do not actually occur, but in whichever direction we contemplate a reversible process we can by a small change in the conditions produce a natural process differing as little as we choose from the reversible process contemplated.

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* Planck, Ann. Phys. Lpz. 1887 **30** 563.

We shall illustrate the three types by an example. Consider a system consisting of a liquid together with its vapour at a pressure P. Let the equilibrium vapour pressure of the liquid be P_{eq}. Consider now the process of the evaporation of a small quantity of the liquid. If $P < P_{\mathrm{eq}}$, this is a natural process and will in fact take place. If on the other hand $P > P_{\mathrm{eq}}$, the process contemplated is unnatural and cannot take place; in fact the contrary process of condensation will take place. If $P = P_{\mathrm{eq}}$ then the process contemplated and its converse are reversible, for by slightly decreasing or increasing P we can make either occur. The last case may be described in an alternative manner as follows. If $P = P_{\mathrm{eq}} - \delta$, where $\delta > 0$, then the process of evaporation is a natural one. Now suppose δ gradually decreased. In the limit $\delta \to 0$, the process becomes reversible.

§1.13 *Reversible process and reversible change*

We have defined a reversible process as a hypothetical passage through equilibrium states. If we have a system interacting with its surroundings either through the performance of work or through the flow of heat, we shall use the term *reversible process* only if there is throughout the process equilibrium between the system and its surroundings. If we wish to refer to the hypothetical passage of the system through a sequence of internal equilibrium states, without necessarily being in equilibrium with its surroundings we shall refer to a *reversible change.* We shall illustrate this distinction by examples.

Consider a system consisting of a liquid and its vapour in mutual equilibrium in a cylinder closed by a piston opposed by a pressure equal to the equilibrium vapour pressure corresponding to the temperature of the system. Suppose now that there is a flow of heat through the walls of the cylinder, with a consequent evaporation of liquid and work done on the piston at constant temperature and pressure. The change in the system is a reversible change, but the whole process is a reversible process only if the medium surrounding the cylinder is at the same temperature as the liquid and vapour; otherwise the flow of heat through the walls of the cylinder is not reversible and so the process as a whole is not reversible, although the change in the system within the cylinder is reversible.

As a second example consider a flow of heat from one system in complete internal equilibrium to another system in complete internal equilibrium. Provided both systems remain in internal equilibrium then the change which each system undergoes is a reversible change, but the whole process of heat flow is not a reversible process unless the two systems are at the same temperature.

§1.14 *Equilibrium and reversible changes*

If a system is in complete equilibrium, any conceivable infinitesimal change in it must be reversible. For a natural process is an approach towards equilibrium, and as the system is already in equilibrium the change cannot be a natural one. Nor can it be an unnatural one, for in that case the opposite infinitesimal change would be a natural one, and this would contradict the supposition that the system is already in equilibrium. The only remaining possibilibity is that, for a system in complete equilibrium any conceivable infinitesimal change must be reversible.

§1.15 *Closed systems and open systems*

A system of fixed material content is called a *closed system* and a system of variable content is called an *open system.* Similarly a phase of fixed content is called a *closed phase* and a phase of variable content is called an *open phase.*

We shall often be concerned with a closed system composed of two or more open phases.

Provided a closed phase is at rest and in thermal equilibrium and provided chemical reactions are excluded, the phase is always in internal equilibrium. As already mentioned in §1.02 it has two degrees of freedom, that is to say one more than a hypothetical hydrostatic fluid having properties independent of temperature. The state of such a phase may therefore be defined by its energy U and its volume V, but other choices are possible.

§1.16 *Entropy*

There exists a function S of the state of a system called the *entropy* of the system having the following properties.

1. The entropy S^{Σ} of a system Σ is the sum of the entropies of its parts, α, β, . . . so that

$$S^{\Sigma}=S^{\alpha}+S^{\beta}+\dots. \qquad 1.16.1$$

In this respect entropy is similar to mass, volume, and energy.

2. The entropy S^{α} of a closed phase α is determined by the energy U^{α} and the volume V^{α} of the phase so that

$$\mathrm{d}S^{\alpha}=(\partial S^{\alpha}/\partial U^{\alpha})_{V^{\alpha}}\mathrm{d}U^{\alpha}+(\partial S^{\alpha}/\partial V^{\alpha})_{U^{\alpha}}\mathrm{d}V^{\alpha}. \qquad 1.16.2$$

3. $(\partial S^{\alpha}/\partial U^{\alpha})_{V^{\alpha}}$ is always positive. 1.16.3

4. The entropy of an insulated closed system Σ increases in any natural

change, remains constant in any reversible change, and is a maximum at equilibrium. Hence

$$dS^{\Sigma} \geqq 0 \qquad \text{(insulated closed system).} \qquad 1.16.4$$

5. In any reversible adiabatic change the entropy remains constant. Thus

$$dS^{\Sigma} = 0 \qquad \text{(reversible adiabatic).} \qquad 1.16.5$$

These properties together determine the entropy completely except for an additive constant to which any conventional value may be assigned.

§1.17 *Thermal equilibrium*

Consider a thermally insulated system composed of two closed phases each maintained at constant volume and in thermal contact with each other. Using the superscript $^{\Sigma}$ to denote the system and the superscripts $^{\alpha}$ and $^{\beta}$ to denote the two phases we have

$$dV^{\alpha} = 0 \qquad dV^{\beta} = 0 \qquad 1.17.1$$

$$dU^{\Sigma} = dU^{\alpha} + dU^{\beta} = 0 \qquad 1.17.2$$

$$dS^{\Sigma} = dS^{\alpha} + dS^{\beta} \geqq 0 \qquad 1.17.3$$

the inequality holding for a natural heat flow and the equality for a reversible heat flow. By virtue of (1) we may rewrite (3) as

$$(\partial S^{\alpha}/\partial U^{\alpha})_{V^{\alpha}} dU^{\alpha} + (\partial S^{\beta}/\partial U^{\beta})_{V^{\beta}} dU^{\beta} \geqq 0 \qquad 1.17.4$$

and by virtue of (2) this becomes

$$\{(\partial S^{\alpha}/\partial U^{\alpha})_{V^{\alpha}} - (\partial S^{\beta}/\partial U^{\beta})_{V^{\beta}}\} dU^{\alpha} \geqq 0. \qquad 1.17.5$$

We now define a positive quantity T by

$$T = (\partial U/\partial S)_V = 1/(\partial S/\partial U)_V \qquad 1.17.6$$

and rewrite (5) as

$$(1/T^{\alpha} - 1/T^{\beta}) dU^{\alpha} \geqq 0 \qquad 1.17.7$$

which is equivalent to

$$(T^{\beta} - T^{\alpha}) dU^{\alpha} \geqq 0. \qquad 1.17.8$$

Hence for a natural process $dU^{\alpha} = -dU^{\beta}$ has the same sign as $T^{\beta} - T^{\alpha}$.

§1.18 *Thermodynamic temperature*

The property of T expressed by formula (1.17.8) is obviously that of a temperature and T defined by formula (1.17.6) is called *thermodynamic* *temperature*. This temperature is independent of any particular property of any particular substance. It will be used throughout this book and will be referred to simply as *temperature*.

§1.19 *Entropy and heat*

For a single closed phase α we have

$$\mathrm{d}S^\alpha = (\partial S^\alpha/\partial U^\alpha)_{V^\alpha}\mathrm{d}U^\alpha + (\partial S^\alpha/\partial V^\alpha)_{U^\alpha}\mathrm{d}V^\alpha \qquad 1.19.1$$

and conversely if we regard U^α as a function of S^α and V^α

$$\begin{aligned}\mathrm{d}U^\alpha &= (\partial U^\alpha/\partial S^\alpha)_{V^\alpha}\mathrm{d}S^\alpha + (\partial U^\alpha/\partial V^\alpha)_{S^\alpha}\mathrm{d}V^\alpha \\ &= T^\alpha\,\mathrm{d}S^\alpha + (\partial U^\alpha/\partial V^\alpha)_{S^\alpha}\mathrm{d}V^\alpha.\end{aligned} \qquad 1.19.2$$

We recall that for a reversible adiabatic change S^α remains constant and consequently

$$\mathrm{d}U^\alpha = (\partial U^\alpha/\partial V^\alpha)_{S^\alpha}\mathrm{d}V^\alpha = w = -P^\alpha\mathrm{d}V^\alpha \qquad (S^\alpha = \text{const.}) \qquad 1.19.3$$

where P^α denotes the pressure of the phase α. Hence

$$(\partial U^\alpha/\partial V^\alpha)_{S^\alpha} = -P^\alpha \qquad 1.19.4$$

and substituting (4) into (2) we obtain

$$\mathrm{d}U^\alpha = T^\alpha\,\mathrm{d}S^\alpha - P^\alpha\mathrm{d}V^\alpha. \qquad 1.19.5$$

Comparing this with the statement of the first law

$$\mathrm{d}U^\alpha = q + w = q - P^\alpha\mathrm{d}V^\alpha \qquad 1.19.6$$

we see that for a reversible change

$$T^\alpha\,\mathrm{d}S^\alpha = q. \qquad 1.19.7$$

We shall now study the change in entropy when the system is neither thermally insulated nor in complete internal equilibrium. Let the system Σ be composed of phases α, β, . . . each in internal equilibrium. If two or more parts of the system Σ have the same composition but different temperatures these are to be regarded as different phases. Now consider an infinitesimal change in Σ in which the quantities of heat gained by the phases α, β, . . . are q^α, q^β, ... Evidently the changes inside the system Σ are independent of where the heat q^α, q^β, . . . comes from or where the heat $-q^\alpha$, $-q^\beta$, . . . goes to. We may therefore without affecting the changes inside Σ arrange for α to exchange heat only with a system α′ which is in internal equilibrium and has the same temperature T^α as α; and similarly for β, ... We also arrange for the composite system $\Sigma+\alpha'+\beta'+..$ to be thermally insulated. We accordingly have

$$dS^{\Sigma}+dS^{\alpha'}+dS^{\beta'}+\ldots\geqq 0. \qquad 1.19.8$$

We also have

$$\begin{aligned} dS^{\alpha'}&=q^{\alpha'}/T^{\alpha'}=-q^{\alpha}/T^{\alpha}\\ dS^{\beta'}&=q^{\beta'}/T^{\beta'}=-q^{\beta}/T^{\beta}\end{aligned} \qquad 1.19.9$$

and so on. Substituting (9) into (8) we obtain

$$dS^{\Sigma}\geqq q^{\alpha}/T^{\alpha}+q^{\beta}/T^{\beta}+\ldots. \qquad 1.19.10$$

In particular for any single phase α

$$dS^{\alpha}\geqq q^{\alpha}/T^{\alpha} \qquad 1.19.11$$

the inequality relating to a natural change and the equality to a reversible change.

The property of entropy described by (11) may alternatively be expressed as follows*

$$dS^{\alpha}=d_eS^{\alpha}+d_iS^{\alpha} \qquad 1.19.12$$

$$d_eS^{\alpha}=q^{\alpha}/T^{\alpha} \qquad 1.19.13$$

$$d_iS^{\alpha}\geqq 0 \qquad 1.19.14$$

where d_eS^{α} denotes the increase in S^{α} associated with interaction of α with its surroundings and d_iS^{α} denotes the increase in S^{α} associated with a natural change occurring inside α.

§1.20 *Second law*

The enunciation of the properties of entropy and of thermodynamic temperature together constitute the *second law* of thermodynamics. The second law was foreshadowed by the work of Carnot† (1824). The first and second laws were co-ordinated by Clausius‡ (1850) and by Kelvin§ (1851).

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* Prigogine and Defay, Chemical Thermodynamics, English translation by Everett, Longmans 1954 ch. 3.

† Carnot, Réflexions sur la puissance motrice du feu, Bachelier, Paris, 1824. Reprinted in 1912 by Hermann, Paris and in 1953 by Blanchard, Paris, together with some notes discovered after Carnot's death in 1832 and communicated to the Académie des Sciences in 1878 by Carnot's brother.

‡ Clausius, Ann. Phys. Lpz. 1850 **79** 368, 500.

§ W. Thomson, Trans. Roy. Soc. Edinb. 1853 **20** 261.

Thermodynamic temperature was introduced by Kelvin* (1848). The conception of *entropy* was first used by Clausius† in 1854 and the name also by Clausius‡ in 1865. The formulation used above follows closely that of Callen§ (1961).

§1.21 *Units*

The unit of energy in the 'Système International' is the *joule* denoted by J and defined by $\mathrm{J} = \mathrm{kg\,m^2\,s^{-2}}$. Another unit still widely used by physical chemists is the thermochemical calorie denoted by cal and defined by cal = 4.184 J exactly.

The unit of thermodynamic temperature in the 'Système International' is the *degree Kelvin* denoted by K and defined by the statement that the thermodynamic temperature T_{tp} of the triple point of natural water is 273.16 K exactly‖. The normal freezing point of water, defined as the freezing point of water saturated with air at atmospheric pressure, is within the accuracy of experiment 273.150 K. The normal boiling point of water, defined as the boiling point at a pressure of one atmosphere, is within the accuracy of experiment 373.15 K. The Celsius scale of temperature denoted by °C is defined by

$$x\ ^\circ\mathrm{C} = (273.150 + x)\mathrm{K}.$$

In physical chemistry the commonest unit of pressure is the atmosphere denoted by atm and defined‖ by $\mathrm{atm} = 1.01325 \times 10^5\,\mathrm{J\,m^{-3}}$ exactly.

§1.22 *Extensive properties*

The mass of a system is clearly equal to the sum of the masses of its constituent phases. Any property, such as mass, whose value for the whole system is equal to the sum of its values for the separate phases is called an *extensive property*.

Important examples of extensive properties are the energy U, the entropy S, and the volume V. The energy U^Σ of a system Σ is related to the energies U^α of the separate phases α by

$$U^\Sigma = \sum_\alpha U^\alpha. \qquad 1.22.1$$

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[*] W. Thomson, Proc. Cambridge Phil. Soc. 1848 **1** 69.

[†] Clausius, Ann. Phys. Lpz. 1854 **93** 481.

[‡] Clausius, Ann. Phys. Lpz. 1865 **125** 353.

[§] Callen, Thermodynamics, Wiley 1961; Guggenheim, Proc. Phys. Soc. London 1962 **79** 1079.

[‖] C. R. Conférence Générale des Poids et Mesures 1954.

Similarly, for the entropy, we have

$$S^{\Sigma}=\sum_{\alpha} S^{\alpha} \qquad 1.22.2$$

and for the volume

$$V^{\Sigma}=\sum_{\alpha} V^{\alpha}. \qquad 1.22.3$$

When we are considering a system of one phase only we may obviously omit the superscript and shall sometimes do so.

§1.23 *Intensive properties*

The density of a phase is clearly constant throughout the phase, because the phase is by definition homogeneous. Further, the density of a phase of a given kind and state is independent of the quantity of the phase. Any property of a phase with these characteristics is called an *intensive property.*

The temperature T^{α} and the pressure P^{α} of a phase α are important examples of intensive properties.

§1.24 *Chemical content of phase*

The content of a phase α is defined by the amount n_i^{α} of each of a finite number of *independently variable chemical species* in the phase. The unit of amount might be chosen as the amount having a given mass but this mass would not necessarily be the same mass for different chemical species. In fact, it is usually most convenient to take as unit of amount the *mole*, that is a mass proportional to that given by the accepted chemical formula of the particular species. A purely thermodynamic definition of the mole as unit of amount will be given in §3.13. In anticipation of this we shall use the mole as the unit of amount for each chemical species.

§1.25 *Chemically inert species*

We must emphasize that in the previous section we specified that the chemical species by which the chemical content of the phase is described must be *independently variable.* In the absence of any chemical reaction there is no difficulty, but if some of the species can react chemically the recipe required for selecting a set of *independently variable* species is not so simple. In order to postpone this complication we shall exclude the possibility of chemical reactions until we come to §1.43 when we revert to the subject.

§1.26 *Partial and proper quantities*

We have seen that the state of a closed phase α may be completely defined by its energy U^α and its volume V^α, or by its entropy S^α and its volume V^α. It follows that an open phase may be completely defined by U^α, V^α, and the amount n_i^α of each chemical species i, or alternatively by S^α, V^α, and the n_i^α's. But other choices are possible such as T^α, V^α, and the n_i^α's. In particular the set T^α, P^α, and the n_i^α's is especially convenient.

Now let X^α denote any extensive property of the phase α such as V^α or U^α or S^α. Then we can derive intensive properties, which we denote by X_i^α, defined by

$$X_i^\alpha = (\partial X^\alpha/\partial n_i^\alpha)_{T,P,n_j^\alpha} \qquad (j \neq i). \qquad 1.26.1$$

We shall call V_i^α the *partial volume*, U_i^α the *partial energy*, and S_i^α the *partial entropy*, and so on, of the species i in the phase α.

At given temperature and pressure we have then

$$\mathrm{d}X^\alpha = \sum_i (\partial X^\alpha/\partial n_i^\alpha)\mathrm{d}n_i^\alpha = \sum_i X_i^\alpha \mathrm{d}n_i^\alpha \qquad (\text{const. } T, P). \qquad 1.26.2$$

Since X^α is homogeneous of first degree in the n_i^α's we have by Euler's theorem

$$X^\alpha = \sum_i n_i^\alpha(\partial X^\alpha/\partial n_i^\alpha) = \sum_i n_i^\alpha X_i^\alpha. \qquad 1.26.3$$

We may accordingly regard X^α as made up additively by a contribution X_i^α from each unit amount of i.

We also define another intensive property X_m^α by the formula

$$X_\mathrm{m}^\alpha = X^\alpha/\sum_i n_i^\alpha = \sum_i n_i^\alpha X_i^\alpha/\sum_i n_i^\alpha. \qquad 1.26.4$$

We call V_m^α the *proper volume* of the phase α; we call U_m^α the *proper energy* of the phase α, and we call S_m^α the *proper entropy* of the phase α.

In the simple case of only a single chemical species i we have

$$X_i^\alpha = X_\mathrm{m}^\alpha = X^\alpha/n_i^\alpha \qquad (\text{single species}). \qquad 1.26.5$$

We emphasize that whereas V^α, U^α, S^α, and any other X^α are extensive properties, V_i^α, U_i^α, S_i^α, and any other X_i^α are intensive properties. Since n_i^α is normally measured in moles it follows that V_i^α and V_m^α would be measured in $\mathrm{m}^3\mathrm{mole}^{-1}$ or $\mathrm{cm}^3\mathrm{mole}^{-1}$, U_i^α and U_m^α in $\mathrm{J\,mole}^{-1}$ or $\mathrm{cal\,mole}^{-1}$, and S_i^α and S_m^α in $\mathrm{J\,K}^{-1}\,\mathrm{mole}^{-1}$ or $\mathrm{cal\,K}^{-1}\,\mathrm{mole}^{-1}$.

Corresponding to every equation homogeneous of the first degree in the extensive variables there is an analogous equation between the partial quantities and another analogous equation between the proper quantities. For example from the fundamental equation for a closed phase

$$\mathrm{d}U^{\alpha}=T^{\alpha}\mathrm{d}S^{\alpha}-P^{\alpha}\mathrm{d}V^{\alpha} \tag{1.26.6}$$

we obtain by differentiating with respect to n_i^{α}

$$\mathrm{d}U_i^{\alpha}=T^{\alpha}\mathrm{d}S_i^{\alpha}-P^{\alpha}\mathrm{d}V_i^{\alpha} \tag{1.26.7}$$

whereas by dividing by $\Sigma_i\, n_i^{\alpha}$ we obtain

$$\mathrm{d}U_{\mathrm{m}}^{\alpha}=T^{\alpha}\mathrm{d}S_{\mathrm{m}}^{\alpha}-P^{\alpha}\mathrm{d}V_{\mathrm{m}}^{\alpha}. \tag{1.26.8}$$

It is perhaps worth while drawing attention here to the fact that the quantity X need not be a thermodynamic property of the system. It is only required that X shall be an extensive property. We shall merely mention one example of such a non-thermodynamic property. If r denotes the refractive index of a binary mixture, we define the *total refractivity* R of the system by

$$R=(r^2-1)V/(r^2+2) \tag{1.26.9}$$

so that R is clearly an extensive property. We then define *partial refractivities* in the usual way by

$$R_1=(\partial R/\partial n_1)_{T,P,n_2} \tag{1.26.10}$$

$$R_2=(\partial R/\partial n_2)_{T,P,n_1} \tag{1.26.11}$$

and it then follows as usual that

$$R=n_1 R_1+n_2 R_2. \tag{1.26.12}$$

The reason for choosing this particular example is the following. There are theoretical grounds for expecting R to be an approximately additive quantity, in which case R_1, R_2 would be independent of the composition of the mixture and have the same values as for the two pure substances. This is more or less supported by experiment. There are however theoretical grounds for expecting in certain cases deviations from simple additivity and this is also confirmed by experiment. The quantitative theoretical discussion of such deviations from simple additivity could be improved by the use of the partial refractivities defined as above.

§1.27 *Chemical potentials*

We recall formula (1.19.5) for a closed phase α at temperature T and pressure P

$$\mathrm{d}U^{\alpha}=T\,\mathrm{d}S^{\alpha}-P\,\mathrm{d}V^{\alpha} \qquad \text{(closed phase).} \tag{1.27.1}$$

This may be extended to an open phase in the form

$$\mathrm{d}U^\alpha = T\mathrm{d}S^\alpha - P\mathrm{d}V^\alpha + \sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha \qquad \text{(open phase)} \qquad 1.27.2$$

where each μ_i^α is defined by

$$\mu_i^\alpha = (\partial U^\alpha / \partial n_i^\alpha)_{S^\alpha, V^\alpha, n_j^\alpha} \qquad (j \neq i). \qquad 1.27.3$$

μ_i^α is called the *chemical potential* of the species i in the phase α. The dimensions of μ_i^α are energy/amount and it is therefore an intensive quantity.

§1.28 *Characteristic functions. Fundamental equations*

Formula (1.27.2)

$$\mathrm{d}U^\alpha = T\mathrm{d}S^\alpha - P\mathrm{d}V^\alpha + \sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha \qquad 1.28.1$$

relates U^α to the independent variables S^α, V^α, and the n_i^α's, and U^α is said to be a *characteristic function* for these variables. Characteristic functions for other variables are readily obtained by the device known as a *Legendre transformation**. In particular

$$\mathrm{d}(U^\alpha - TS^\alpha) = -S^\alpha \mathrm{d}T - P\mathrm{d}V^\alpha + \sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha \qquad 1.28.2$$

$$\mathrm{d}(U^\alpha + PV^\alpha) = T\mathrm{d}S^\alpha + V^\alpha \mathrm{d}P + \sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha \qquad 1.28.3$$

$$\mathrm{d}(U^\alpha - TS^\alpha + PV^\alpha) = -S^\alpha \mathrm{d}T + V^\alpha \mathrm{d}P + \sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha. \qquad 1.28.4$$

Since these formulae are all homogeneous of first degree in U^α, S^α, V^α, n_i^α, it follows by Euler's theorem that

$$U^\alpha - TS^\alpha + PV^\alpha = \sum_i n_i^\alpha \mu_i^\alpha. \qquad 1.28.5$$

The quantity $U^\alpha - TS^\alpha$ on the left of (2) is called the *Helmholtz function* and will be denoted by $\mathcal{A}^\alpha$. The quantity $U^\alpha + PV^\alpha$ on the left of (3) is denoted by H^α and is called *enthalpy*; this name was first proposed by Kamerlingh Onnes†. The quantity $U^\alpha - TS^\alpha + PV^\alpha$ on the left of (4) is called the *Gibbs function* and is denoted by G^α. Using this notation we have the set of formulae

$$\mathrm{d}U^\alpha = T\mathrm{d}S^\alpha - P\mathrm{d}V^\alpha + \sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha \qquad 1.28.6$$

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* Courant and Hilbert, Methoden der Mathematischen Physik, Springer 1937 §1.6.

† Porter, Trans. Faraday Soc. 1922 **18** 140.

$$\mathrm{d}\mathit{\AE}^{\alpha}=-S^{\alpha}\mathrm{d}T-P\mathrm{d}V^{\alpha}+\sum_{i}\mu_{i}^{\alpha}\mathrm{d}n_{i}^{\alpha} \qquad 1.28.7$$

$$\mathrm{d}H^{\alpha}=T\mathrm{d}S^{\alpha}+V^{\alpha}\mathrm{d}P+\sum_{i}\mu_{i}^{\alpha}\mathrm{d}n_{i}^{\alpha} \qquad 1.28.8$$

$$\mathrm{d}G^{\alpha}=-S^{\alpha}\mathrm{d}T+V^{\alpha}\mathrm{d}P+\sum_{i}\mu_{i}^{\alpha}\mathrm{d}n_{i}^{\alpha} \qquad 1.28.9$$

$$G^{\alpha}=\sum_{i}n_{i}^{\alpha}\mu_{i}^{\alpha}. \qquad 1.28.10$$

Whereas U^{α} is a characteristic function for the independent variables S^{α}, V^{α}, n_{i}^{α}, we see that $\mathit{\AE}^{\alpha}$ is a characteristic function for T, V^{α}, n_{i}^{α}; so is H^{α} for S^{α}, P, n_{i}^{α}, and so is G^{α} for T, P, n_{i}^{α}.

By comparison of (9) with (1.26.1) or (10) with (1.26.3) we see that

$$\mu_{i}^{\alpha}=G_{i}^{\alpha}. \qquad 1.28.11$$

Thus in each phase the chemical potential of each species i is equal to the partial Gibbs function of this species.

The equations (6) to (9) are called *fundamental equations* for the four sets of variables S, V, n_{i}; T, V, n_{i}; S, P, n_{i}; T, P, n_{i}. The four characteristic functions U, $\mathit{\AE}$, H, and G were introduced by Gibbs who denoted them by ε, ψ, χ, and ζ respectively.

The characteristic functions U, $\mathit{\AE}$, H, and G are sufficient for all requirements. They are however not the only possible ones. For example by simple transformation of (6) we have

$$\mathrm{d}S^{\alpha}=T^{-1}\mathrm{d}U^{\alpha}+T^{-1}P\mathrm{d}V^{\alpha}-T^{-1}\sum_{i}\mu_{i}^{\alpha}\mathrm{d}n_{i}^{\alpha} \qquad 1.28.12$$

showing that S^{α} is a characteristic function for the variables U^{α}, V^{α}, n_{i}^{α}. Again let us define two new quantities J and Y by

$$J=S-U/T=-\mathit{\AE}/T \qquad 1.28.13$$

$$Y=S-U/T-PV/T=-G/T. \qquad 1.28.14$$

We now differentiate (13) and (14) and substitute for $\mathrm{d}S^{\alpha}$ from (12) obtaining

$$\mathrm{d}J^{\alpha}=T^{-2}U^{\alpha}\mathrm{d}T+T^{-1}P\mathrm{d}V^{\alpha}-T^{-1}\sum_{i}\mu_{i}\mathrm{d}n_{i}^{\alpha} \qquad 1.28.15$$

$$\mathrm{d}Y^{\alpha}=T^{-2}H^{\alpha}\mathrm{d}T-T^{-1}V^{\alpha}\mathrm{d}P-T^{-1}\sum_{i}\mu_{i}\mathrm{d}n_{i}^{\alpha} \qquad 1.28.16$$

from which we see that J^{α}, like $\mathit{\AE}^{\alpha}$, is a *characteristic function* for the variables T, V^{α}, n_{i}^{α}, and that Y^{α}, like G^{α}, is one for the variables T, P, n_{i}^{α}.

The functions J and Y were introduced by Massieu* (1869) and the latter was widely used by Planck†. We accordingly call J the *Massieu function* and Y the *Planck function.* It is interesting to note that these characteristic functions are six years older than $A\!\!F$ and G introduced by Gibbs.

By means of a *fundamental equation* all the thermodynamic functions can be expressed in terms of the characteristic function and its derivatives with respect to the corresponding independent variables. For example choosing $G^{\alpha}(T, P, n_i^{\alpha})$ we obtain directly from (4)

$$S^{\alpha} = -\partial G^{\alpha}/\partial T \qquad 1.28.17$$

$$H^{\alpha} = G^{\alpha} - T\partial G^{\alpha}/\partial T \qquad 1.28.18$$

$$V^{\alpha} = \partial G^{\alpha}/\partial P \qquad 1.28.19$$

$$U^{\alpha} = G^{\alpha} - T\partial G^{\alpha}/\partial T - P\partial G^{\alpha}/\partial P \qquad 1.28.20$$

$$\mu_i^{\alpha} = \partial G^{\alpha}/\partial n_i^{\alpha} \qquad 1.28.21$$

$$\partial\mu_i^{\alpha}/\partial T = \partial^2 G^{\alpha}/\partial n_i^{\alpha}\partial T = \partial^2 G^{\alpha}/\partial T\partial n_i^{\alpha} = -\partial S^{\alpha}/\partial n_i^{\alpha} = -S_i^{\alpha} \qquad 1.28.22$$

$$\partial\mu_i^{\alpha}/\partial P = \partial^2 G^{\alpha}/\partial n_i^{\alpha}\partial P = \partial^2 G^{\alpha}/\partial P\partial n_i^{\alpha} = \partial V^{\alpha}/\partial n_i^{\alpha} = V_i^{\alpha} \qquad 1.28.23$$

$$\partial(\mu_i^{\alpha}/T)/\partial T = -S_i^{\alpha}/T - \mu_i^{\alpha}/T^2 = -H_i^{\alpha}/T^2. \qquad 1.28.24$$

§1.29 *Mole fractions*

We are often interested only in the intensive properties of a phase and not at all in the amount of the phase. It is then convenient to describe the phase entirely by intensive variables. The set of variables commonly used is T, P, x_i where x_i denotes the *mole fraction* defined by

$$x_i = n_i/\sum_k n_k \qquad 1.29.1$$

where Σ_k denotes summation over all the species.

By definition the mole fractions satisfy the identity

$$\sum_i x_i = 1. \qquad 1.29.2$$

If the number of independent species or *components* is c, then of the c+2 quantities T, P, x_i used to describe the state of the phase, apart from its amount, only c+1 are independent owing to (2). We therefore say that a single phase of c components has c+1 *degrees of freedom.*

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* Massieu, C.R. Acad. Sci., Paris 1869 **69** 858.

† Planck, Treatise on Thermodynamics, translated by Ogg, Longmans, 3rd ed. 1927.

§1.30 *Gibbs–Duhem relation*

We may, if we choose, describe the state of a single phase α, apart from its size, by the set of intensive quantities T, P, μ_i^α. The number of these is c+2. We have however seen that the number of degrees of freedom of a single phase is only c+1. It follows that T, P, μ_i^α cannot be independently variable, but there must be some relation between them corresponding to the identity between mole fractions. We shall now derive such a relation.

We differentiate (1.28.10) and obtain

$$\mathrm{d}G^\alpha=\sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha+\sum_i n_i^\alpha \mathrm{d}\mu_i^\alpha. \qquad 1.30.1$$

From (1) we subtract (1.28.9) and obtain

$$S^\alpha \mathrm{d}T-V^\alpha \mathrm{d}P+\sum_i n_i^\alpha \mathrm{d}\mu_i^\alpha=0. \qquad 1.30.2$$

This is the sought relation between T, P, and the μ_i^α's. It is known as the *Gibbs–Duhem relation**. It is particularly useful in its application to changes at constant temperature and pressure, when it may be written

$$\sum_i x_i^\alpha \mathrm{d}\mu_i^\alpha=0 \qquad (T, P\ \text{const.}). \qquad 1.30.3$$

§1.31 *Multiphase systems*

In the preceding sections most of the formulae have been written explicitly for a single phase. Corresponding formulae for a system Σ consisting of several phases are obtained by summation over all the phases. In particular from the fundamental equations in §1.28 we obtain

$$\mathrm{d}U^\Sigma=\sum_\alpha T^\alpha \mathrm{d}S^\alpha-\sum_\alpha P^\alpha \mathrm{d}V^\alpha+\sum_\alpha\sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha \qquad 1.31.1$$

$$\mathrm{d}\mathcal{F}^\Sigma=-\sum_\alpha S^\alpha \mathrm{d}T^\alpha-\sum_\alpha P^\alpha \mathrm{d}V^\alpha+\sum_\alpha\sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha \qquad 1.31.2$$

$$\mathrm{d}H^\Sigma=\sum_\alpha T^\alpha \mathrm{d}S^\alpha+\sum_\alpha V^\alpha \mathrm{d}P^\alpha+\sum_\alpha\sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha \qquad 1.31.3$$

$$\mathrm{d}G^\Sigma=-\sum_\alpha S^\alpha \mathrm{d}T^\alpha+\sum_\alpha V^\alpha \mathrm{d}P^\alpha+\sum_\alpha\sum_i \mu_i^\alpha \mathrm{d}n_i^\alpha \qquad 1.31.4$$

where Σ_i denotes summation over the components and Σ_α denotes summation over the phases.

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* Gibbs, Collected Works, Longmans, vol. **1**, p. 88; Duhem, Le Potentiel Thermodynamique et ses Applications 1886, p. 33. The reference given by Hildebrand and Scott, Solubility of Nonelectrolytes, Reinhold 1950, is spurious.

We are still postulating the absence of chemical reactions. This restriction will be removed in §1.43 and §1.44.

§1.32 *Adiabatic changes in closed system*

We recall that for any infinitesimal change in a closed system Σ

$$\mathrm{d}U^{\Sigma}=w+q. \qquad 1.32.1$$

If the change is *adiabatic*, then by definition

$$q=0, \qquad \mathrm{d}U^{\Sigma}=w \qquad \text{(adiabatic)}. \qquad 1.32.2$$

All infinitesimal adiabatic changes can moreover, according to the definitions in §1.13 and §1.19, be classified as follows:

$$\mathrm{d}U^{\Sigma}=w, \qquad \mathrm{d}S^{\Sigma}>0 \qquad \text{(natural adiabatic)} \qquad 1.32.3$$

$$\mathrm{d}U^{\Sigma}=w, \qquad \mathrm{d}S^{\Sigma}=0 \qquad \text{(reversible adiabatic)}. \qquad 1.32.4$$

Suppose now that the whole system is enclosed by fixed rigid walls, so that $w=0$. We then have the classification

$$\mathrm{d}U^{\Sigma}=0 \qquad \mathrm{d}V^{\Sigma}=0 \qquad \mathrm{d}S^{\Sigma}>0 \qquad \text{(natural adiabatic)} \qquad 1.32.5$$

$$\mathrm{d}U^{\Sigma}=0 \qquad \mathrm{d}V^{\Sigma}=0 \qquad \mathrm{d}S^{\Sigma}=0 \qquad \text{(reversible adiabatic)}. \qquad 1.32.6$$

Suppose now, instead, that each phase α is partly bounded by a piston acting against a constant pressure P^{α}, so that

$$w=-\sum_{\alpha} P^{\alpha}\mathrm{d}V^{\alpha}=-\sum_{\alpha}\mathrm{d}(P^{\alpha}V^{\alpha})=-\mathrm{d}(\sum_{\alpha} P^{\alpha}V^{\alpha}). \qquad 1.32.7$$

Then we have

$$\mathrm{d}U^{\Sigma}=-\mathrm{d}(\sum_{\alpha} P^{\alpha}V^{\alpha}) \qquad 1.32.8$$

$$\mathrm{d}H^{\Sigma}=\mathrm{d}(U^{\Sigma}+\sum_{\alpha} P^{\alpha}V^{\alpha})=0. \qquad 1.32.9$$

Consequently in this case we have the classification

$$\mathrm{d}H^{\Sigma}=0 \qquad \mathrm{d}P^{\alpha}=0 \qquad \mathrm{d}S^{\Sigma}>0 \qquad \text{(natural adiabatic)} \qquad 1.32.10$$

$$\mathrm{d}H^{\Sigma}=0 \qquad \mathrm{d}P^{\alpha}=0 \qquad \mathrm{d}S^{\Sigma}=0 \qquad \text{(reversible adiabatic)}. \qquad 1.32.11$$

§1.33 *Isothermal changes in closed systems*

Instead of a thermally insulated system, let us now consider a system whose temperature T is kept uniform and constant. This may be achieved by keeping the system in a temperature bath at the temperature T. Then according to the properties of entropy expounded in §1.19 and in particular formula (1.19.11) we have the classification of infinitesimal changes

$$\mathrm{d}T=0 \qquad \mathrm{d}(TS)^{\Sigma}>q \qquad \text{(natural isothermal)} \tag{1.33.1}$$

$$\mathrm{d}T=0 \qquad \mathrm{d}(TS)^{\Sigma}\doteq q \qquad \text{(reversible isothermal).} \tag{1.33.2}$$

We also have according to the first law of thermodynamics, in particular formula (1.10.7),

$$q=\mathrm{d}U^{\Sigma}-w. \tag{1.33.3}$$

Substituting from (3) into (1) and (2) in turn we obtain

$$\mathrm{d}T=0 \qquad w>\mathrm{d}\mathcal{F}^{\Sigma} \qquad \text{(natural isothermal)} \tag{1.33.4}$$

$$\mathrm{d}T=0 \qquad w=\mathrm{d}\mathcal{F}^{\Sigma} \qquad \text{(reversible isothermal).} \tag{1.33.5}$$

In particular if the system is enclosed by fixed rigid walls, so that $w=0$, the classification becomes

$$\mathrm{d}T=0 \qquad \mathrm{d}V=0 \qquad \mathrm{d}\mathcal{F}^{\Sigma}<0 \qquad \text{(natural isothermal)} \tag{1.33.6}$$

$$\mathrm{d}T=0 \qquad \mathrm{d}V=0 \qquad \mathrm{d}\mathcal{F}^{\Sigma}=0 \qquad \text{(reversible isothermal).} \tag{1.33.7}$$

If on the other hand each phase α is partly bounded by a piston acting against a constant pressure P^{α}, then

$$\begin{aligned} w&=-\sum_{\alpha}P^{\alpha}\mathrm{d}V^{\alpha}=-\sum_{\alpha}\mathrm{d}(P^{\alpha}V^{\alpha})=-\mathrm{d}(\sum_{\alpha}P^{\alpha}V^{\alpha})\\ &=\mathrm{d}(\mathcal{F}-G)^{\Sigma} \end{aligned} \tag{1.33.8}$$

from the definition of G. Substituting from (8) into (4) and (5), we obtain

$$\mathrm{d}T=0 \qquad \mathrm{d}P^{\alpha}=0 \qquad \mathrm{d}G^{\Sigma}<0 \qquad \text{(natural isothermal)} \tag{1.33.9}$$

$$\mathrm{d}T=0 \qquad \mathrm{d}P^{\alpha}=0 \qquad \mathrm{d}G^{\Sigma}=0 \qquad \text{(reversible isothermal).} \tag{1.33.10}$$

§1.34 *Equilibrium conditions. General form*

We saw in §1.14 that if a system is in complete equilibrium then any conceivable change in it must be reversible. This enables us to put the conditions for equilibrium into various forms each of general validity.

If we first consider an infinitesimal change at constant volume, the system being thermally insulated, we have according to (1.32.6) the equilibrium conditions

$$\mathrm{d}S^{\Sigma}=0 \qquad \mathrm{d}V^{\Sigma}=0 \qquad \mathrm{d}U^{\Sigma}=0. \tag{1.34.1}$$

If instead we consider an infinitesimal change keeping each phase α at constant pressure P^{α}, the whole system being thermally insulated, we have according to (1.32.11) the equilibrium conditions

$$dS^{\Sigma}=0 \qquad dP^{\alpha}=0 \qquad dH^{\Sigma}=0. \qquad 1.34.2$$

Thirdly let us consider an infinitesimal change at constant volume and constant uniform temperature (isothermal change). We now have according to (1.33.7) the equilibrium conditions

$$dT=0 \qquad dV^{\Sigma}=0 \qquad d\mathscr{F}^{\Sigma}=0. \qquad 1.34.3$$

Lastly by considering an infinitesimal change keeping each phase at a constant pressure P^{α} and a constant uniform temperature T, we have according to (1.33.10) the equilibrium conditions

$$dT=0 \qquad dP^{\alpha}=0 \qquad dG^{\Sigma}=0. \qquad 1.34.4$$

Any one of the four sets of equilibrium conditions (1), (2), (3), (4) is sufficient by itself. They are all equivalent and each has an equal claim to be regarded as fundamental.

§1.35 *Stability and metastability*

In order to make clear what is meant by stability and instability in thermodynamic systems, we shall first discuss the significance of these expressions in a purely mechanical system. To this end, in figure 1.1 are shown in section three different equilibrium positions of a box on a stand. In positions *a* and *c* the centre of gravity G is lower than in any infinitesimally distant position, consistent with the box resting on the stand; the gravitational potential energy is a minimum, and the equilibrium is stable. If the position of the box be very slightly disturbed, it will of itself return to its former position. In position *b*, on the other hand, the centre of gravity G is higher

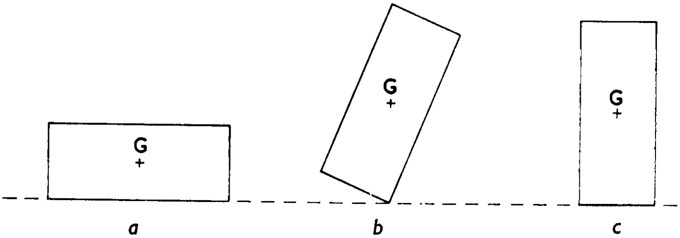

Fig. 1.1. Stable and unstable equilibrium

than in any infinitely near position, consistent with the box resting on the stand, the gravitational potential energy is a maximum, and the equilibrium is unstable. If the position of the box be very slightly disturbed, it will of itself move right away from its original position, and finally settle in some state of stable equilibrium such as *a* or *c*. As maxima and minima of the potential energy must alternate, so must positions of stable and of unstable equilibrium. Only stable equilibria are realizable in practice since the realization of an unstable equilibrium requires the complete absence of any possible disturbing factors.

Whereas positions *a* and *c* are both stable, one may describe *a* as *more stable* than *c*. Or one may say that *a* is *absolutely stable*, while *c* is *unstable compared to a*. By this is meant that in position *c* the potential energy is less than in any position differing only infinitesimally from *c*, but is greater than the potential energy in position *a*.

Similarly, the equilibrium of a thermodynamic system may be *absolutely stable*. On the other hand it may be stable compared with all states differing only infinitesimally from the given state, but unstable compared with some other state differing finitely from the given state; such states are called *metastable*. Truly *unstable* states analogous to *b* are unrealizable in thermodynamics, just as they are in mechanics.

The fact that all thermodynamic equilibria are stable or metastable, but never unstable, is equivalent to the fact that every natural process proceeds towards an equilibrium state, never away from it. Bearing this in mind and referring to the inequalities (1.32.5), (1.32.10), (1.33.6), and (1.33.9), we obtain the following alternative conditions for equilibrium:

for given U^{Σ} and V^{Σ} that S^{Σ} is a *maximum* 1.35.1

for given H^{Σ} and P^{α}'s that S^{Σ} is a *maximum* 1.35.2

for given T and V that $Æ^{\Sigma}$ is a *minimum* or that J^{Σ} is a *maximum* 1.35.3

for given T and P^{α}'s that G^{Σ} is a *minimum* or that Y^{Σ} is a *maximum.* 1.35.4

Since $(\partial U/\partial S)_V = (\partial H/\partial S)_P = T > 0$, we may replace the first two conditions above by two others so as to obtain the more symmetrical set of equivalent conditions

for given S^{Σ} and V^{Σ} that U^{Σ} is a *minimum* 1.35.5

for given S^{Σ} and P^{α}'s that H^{Σ} is a *minimum* 1.35.6

for given T and V^{Σ} that $Æ^{\Sigma}$ is a *minimum* 1.35.7

for given T and P^{α}'s that G^{Σ} is a *minimum.* 1.35.8

Since T is a more convenient independent variable than S, the last two conditions are more useful, but nowise more fundamental, than the previous two.

Each of the above is the condition for stable equilibrium or for metastable equilibrium according as the minimum (or maximum) is absolute or only relative to neighbouring states.

§1.36 *Thermal internal stability*

Consider a closed single phase. Let its entropy be S, its volume V, and its energy U. Imagine one half of the mass of this phase to change so as to have an entropy $\frac{1}{2}(S+\delta S)$ and volume $\frac{1}{2}V$ while the other half changes so as to have an entropy $\frac{1}{2}(S-\delta S)$ and volume $\frac{1}{2}V$. According to Taylor's expansion the energy of the first half becomes

$$\tfrac{1}{2}\{U+(\partial U/\partial S)\delta S+\tfrac{1}{2}(\partial^2 U/\partial S^2)(\delta S)^2\} \qquad 1.36.1$$

when we neglect small quantities of third and higher orders; all partial differentiations in (1) are at constant V. The energy of the second half becomes similarly

$$\tfrac{1}{2}\{U-(\partial U/\partial S)\delta S+\tfrac{1}{2}(\partial^2 U/\partial S^2)(\delta S)^2\}. \qquad 1.36.2$$

Hence by addition the energy of the whole system has increased by the second order small quantity

$$\tfrac{1}{2}(\partial^2 U/\partial S^2)_V(\delta S)^2 \qquad 1.36.3$$

while the total entropy and volume remain unchanged. Now a condition for a system to be in *stable* equilibrium is that, for given values of the entropy and the volume, the energy should be a *minimum*. If then the original state of the system was *stable*, the change considered must lead to an *increase* of energy and the expression (3) must be positive. Hence we obtain as a necessary condition for stable equilibrium

$$(\partial^2 U/\partial S^2)_V>0. \qquad 1.36.4$$

Since according to (1.17.6)

$$(\partial U/\partial S)_V=T \qquad 1.36.5$$

we can replace (4) by

$$(\partial S/\partial T)_V>0. \qquad 1.36.6$$

The physical meaning of (6) is that when at constant volume heat is absorbed by a stable phase its temperature is raised.

§1.37 *Hydrostatic equilibrium*

Consider a system Σ of several phases in equilibrium at the temperature T. Suppose the phase α to increase in volume by an amount $\mathrm{d}V^{\alpha}$ and the phase β to decrease by the same amount, the temperature and volume of the whole system and the composition of each phase remaining unchanged. Then, according to (1.34.3), the condition for equilibrium is

$$\mathrm{d}\mathcal{F}^{\Sigma}=\mathrm{d}\mathcal{F}^{\alpha}+\mathrm{d}\mathcal{F}^{\beta}=0 \qquad 1.37.1$$

or by using (1.28.7)

$$-P^{\alpha}\mathrm{d}V^{\alpha}+P^{\beta}\mathrm{d}V^{\alpha}=0 \qquad 1.37.2$$

and so

$$P^{\alpha}=P^{\beta}. \qquad 1.37.3$$

That is to say that any two phases in hydrostatic equilibrium must be at the same pressure.

If we now consider two phases at the same temperature T and different pressures P^{α} and P^{β}, there will then not be hydrostatic equilibrium. There will be a tendency for the system to approach hydrostatic equilibrium by a change in which the volume of one phase, say α, increases by $\mathrm{d}V^{\alpha}$ and that of the other phase β decreases by the same amount. Such a change is by definition a natural one. If we keep the temperature constant, we therefore have, according to (1.33.6)

$$\mathrm{d}\mathcal{F}^{\alpha}+\mathrm{d}\mathcal{F}^{\beta}<0 \qquad 1.37.4$$

or using (1.28.7)

$$-P^{\alpha}\mathrm{d}V^{\alpha}+P^{\beta}\mathrm{d}V^{\alpha}<0. \qquad 1.37.5$$

If we suppose $\mathrm{d}V^{\alpha}$ to be positive, it follows that

$$P^{\alpha}>P^{\beta}. \qquad 1.37.6$$

That is to say, that the phase α with the greater pressure P^{α} will increase in volume at the expense of the phase β with the smaller pressure P^{β}.

§1.38 *Hydrostatic internal stability*

Consider again a closed single phase. Let its temperature be T, its volume V, its energy U, and its entropy S. Imagine half of the phase to change so as to have a volume $\frac{1}{2}(V+\delta V)$, and the other half to change so as to have a volume $\frac{1}{2}(V-\delta V)$, the temperature remaining uniform and unchanged. Then by an argument precisely analogous to that of the §1.36 we find that the Helmholtz function of the whole system has increased by the second order small quantity

$$\tfrac{1}{2}(\partial^2 \mathcal{F}/\partial V^2)_T(\delta V)^2 \qquad 1.38.1$$

while the temperature and total volume are unchanged. Now a condition for a system to be in *stable* equilibrium is that for given values of temperature and volume, the Helmholtz function should be a *minimum.* If then the original state of the system was *stable,* the change considered must lead to an *increase* of the Helmholtz function and the expression (1) must be positive. Hence we obtain as a necessary condition for stable equilibrium

$$(\partial^2 \mathcal{F}/\partial V^2)_T > 0. \qquad 1.38.2$$

Since according to (1.28.7)

$$(\partial \mathcal{F}/\partial V)_T = -P \qquad 1.38.3$$

we can replace (2) by

$$(\partial V/\partial P)_T < 0. \qquad 1.38.4$$

This means that when the pressure of a stable phase is increased, the volume must decrease.

§1.39 *Equilibrium distribution between phases*

Consider a system of several phases, all at the same temperature T, but not necessarily at the same pressure. Suppose a small amount $\mathrm{d}n_i^\alpha$ of the species i to pass from the phase β to the phase α, the temperature of the whole system being kept constant. Then according to (1.31.2) we have

$$\mathrm{d}\mathcal{F}^\Sigma = -\sum_\gamma P^\gamma \mathrm{d}V^\gamma + \mu_i^\alpha \mathrm{d}n_i^\alpha - \mu_i^\beta \mathrm{d}n_i^\alpha \qquad 1.39.1$$

omitting the terms which obviously vanish. Since the total work w done on the whole system is $-\Sigma_\gamma P^\gamma \mathrm{d}V^\gamma$, it follows from (1.33.4) that the process considered will be a natural one if

$$\mathrm{d}\mathcal{F}^\Sigma < -\sum_\gamma P^\gamma \mathrm{d}V^\gamma \qquad \text{(natural process).} \qquad 1.39.2$$

Comparing (1) with (2) we obtain

$$(\mu_i^\alpha - \mu_i^\beta)\mathrm{d}n_i^\alpha < 0 \qquad \text{(natural process).} \qquad 1.39.3$$

Thus $\mathrm{d}n_i^\alpha$ in a natural process has the same sign as $\mu_i^\beta - \mu_i^\alpha$. In other words each chemical species i tends to move from a phase where its potential μ_i is higher to another phase in which its potential is lower. Hence the name *potential* or *chemical potential* for μ_i.

If, instead of natural processes, we consider reversible processes we have equalities instead of inequalities; in particular instead of (3) we have

$$(\mu_i^\alpha - \mu_i^\beta)\mathrm{d}n_i^\alpha = 0 \qquad \text{(reversible process)} \qquad 1.39.4$$

or

$$\mu_i^\alpha = \mu_i^\beta \qquad \text{(equilibrium).} \qquad 1.39.5$$

We have obtained the important result that the condition for two phases to be in equilibrium with respect to any species is that the chemical potential of that species should have the same value in the two phases.

§1.40 *Phase stability*

Consider again a closed single phase. Let its temperature be T, its pressure P, and its Gibbs function G. Imagine the amount of the component i to increase in one half of the phase from $\frac{1}{2}n_i$ to $\frac{1}{2}(n_i+\delta n_i)$ while the amount in the other half of the phase changes from $\frac{1}{2}n_i$ to $\frac{1}{2}(n_i-\delta n_i)$, the temperature and pressure remaining uniform and unchanged. Then by an argument precisely analogous to those of §1.36 and §1.38 we find that the Gibbs function of the whole system has increased by the second order small quantity

$$\tfrac{1}{2}(\partial^2 G/\partial n_i^2)_{T,P,n_j}(\delta n_i)^2 \qquad (j \neq i) \qquad 1.40.1$$

while the temperature and pressure remain unchanged. Now a condition for a system to be in *stable* equilibrium is that for given values of temperature and pressure, the Gibbs function should be a *minimum*. If then the original state of the system was *stable*, the change considered must lead to an *increase* of the Gibbs function and the expression (1) must be positive. Hence we obtain as a necessary condition for stable equilibrium

$$(\partial^2 G/\partial n_i^2)_{T,P,n_j}(\delta n_i)^2 > 0 \qquad (j \neq i). \qquad 1.40.2$$

Since according to (1.28.9)

$$(\partial G/\partial n_i)_{T,P,n_j} = \mu_i \qquad (j \neq i) \qquad 1.40.3$$

we can replace (2) by

$$(\partial \mu_i/\partial n_i)_{T,P,n_j} > 0 \qquad (j \neq i). \qquad 1.40.4$$

This means that when substance i is added to a stable mixed phase the chemical potential of i is increased.

§1.41 *Gibbs' phase rule*

In §1.30 we mentioned that the state of a single phase α containing c independent species or *components* can, apart from its size, be completely described by the c+2 quantities $T, P, \mu_1, \mu_2, \ldots \mu_c$. Of these c+2 quantities only c+1 are independent because of the Gibbs–Duhem relation

$$S^{\alpha}\mathrm{d}T - V^{\alpha}\mathrm{d}P + \sum_i n_i^{\alpha}\mathrm{d}\mu_i = 0. \qquad 1.41.1$$

We accordingly say that a single phase has c+1 *degrees of freedom.*

We shall now extend this rule to a system of c components in p phases in mutual equilibrium. We continue to use the same c+2 variables but there are now p Gibbs–Duhem relations, one for each phase. Consequently the number of independent variables or the number of *degrees of freedom* is c−p+2. This is Gibbs' phase rule*.

We have implicitly excluded chemical reaction between the species and we postpone discussion of the effect of any such complication to chapter 6.

§1.42 *Membrane equilibrium*

It is important to notice that, provided a system is at a uniform temperature, the condition for equilibrium between two phases of each chemical species is independent of that for other species and of that for hydrostatic equilibrium. If then two phases α and β are separated by a fixed wall permeable to some components *i* but not to other components *j*, the condition for the two phases to be in equilibrium as regards *i* is still

$$\mu_i^{\alpha} = \mu_i^{\beta} \qquad 1.42.1$$

but in this case in general

$$P^{\alpha} \neq P^{\beta} \qquad \mu_j^{\alpha} \neq \mu_j^{\beta}. \qquad 1.42.2$$

Such a partial equilibrium is called a *membrane equilibrium.*

§1.43 *Chemical reactions. Frozen equilibrium*

Hitherto we have explicitly excluded chemically reacting species from the system considered. We shall now explain how this restriction can be removed.

Owing to the slowness of attainment of some chemical equilibria, it can happen that the change towards chemical equilibrium is negligible during a time sufficient for other kinds of equilibrium to be observed and measured. In other cases the attainment of chemical equilibrium if not sufficiently slow for this to be the case can be made so by the addition to the system of a small quantity of a substance called an *anticatalyst* or merely by rigid

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[*] Gibbs, Collected Works, Longmans, vol. 1, p. 96.

exclusion of all traces of some other substance called a *catalyst*. Even in cases where the attainment of chemical equilibrium cannot be adequately slowed down in practice it is possible and legitimate to consider the hypothetical case wherein this has been achieved.

We are thus led to consider a system not in chemical equilibrium in which however the chemical reactions leading towards its attainment have been virtually suppressed. The system is then in a special kind of metastable equilibrium called *frozen equilibrium*. The several chemical species present are then virtually independent and so we can suppose a chemical potential μ assigned to each such species.

If we now suppose the addition of a suitable catalyst so as to *thaw* the *frozen equilibrium* then generally changes of composition will take place as a result of chemical reactions; such changes are of course natural processes. In the special case that the state of frozen equilibrium corresponds to complete chemical equilibrium, then no chemical change will take place on thawing. If we imagine a virtual chemical change to take place, such a change will then be a typical reversible change. If we write down the condition for this, we therefore obtain a relation between the μ's which is a condition of chemical equilibrium.

The final result may be described as follows. Instead of choosing a set of independent chemical species or *components*, we use the set of all the chemical species present whether independent or not and then obtain restrictive relations on their behaviour. The actual form of these restrictive relations will be obtained in the next section.

§1.44 *Chemical equilibrium. Affinity*

We consider a system of any number of phases maintained at a constant temperature T and constant pressure P. Then according to (1.31.4)

$$\mathrm{d}G^{\Sigma}=\sum_{\alpha}\sum_{i}\mu_i^{\alpha}\mathrm{d}n_i^{\alpha} \qquad (T, P \text{ const.}) \qquad 1.44.1$$

where now, in contrast to previous practice, the species i are no longer all incapable of interacting chemically. According to (1.33.9) the condition for a natural process is

$$\mathrm{d}G^{\Sigma}<0 \qquad (T, P \text{ constant}) \qquad (\text{natural process}). \qquad 1.44.2$$

Combining (1) and (2) we obtain as the condition for a natural process

$$\sum_{\alpha}\sum_{i}\mu_i^{\alpha}\mathrm{d}n_i^{\alpha}<0 \qquad (\text{natural process}). \qquad 1.44.3$$

Any chemical reaction at a given temperature and pressure is described by a formula. As typical examples we quote

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$
$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
$$\alpha\text{-glucose(aq)} \rightarrow \beta\text{-glucose(aq)}$$

where (s) denotes a solid phase, (g) the gaseous phase, and (aq) denotes an aqueous solution.

We can represent the most general chemical reaction symbolically by

$$\sum \nu_A A \rightarrow \sum \nu_B B \qquad 1.44.4$$

meaning that ν_A moles of A and the like react together to give ν_B moles of B and the like. The unit of quantity the *mole* is defined in such a way that the *stoichiometric numbers* ν can all be small integers. The symbols A and B are supposed to specify not only the kind of each chemical species i but also in what phase it is present; in other words the label A implies the pair of labels i and α.

Now imagine the chemical process (4) to take place in the time dt to the extent

$$\sum \nu_A \mathrm{d}\xi A \rightarrow \sum \nu_B \mathrm{d}\xi B \qquad 1.44.5$$

where dξ denotes a small number. Then dξ/dt is called the *reaction rate* and the $\mathrm{d}n_i^\alpha$, when i relates to A, is just $-\nu_A \mathrm{d}\xi$. The inequality (3) thus becomes

$$\sum \nu_B \mu_B \mathrm{d}\xi/\mathrm{d}t < \sum \nu_A \mu_A \mathrm{d}\xi/\mathrm{d}t \qquad \text{(natural process)} \qquad 1.44.6$$

or if we assume $\mathrm{d}\xi/\mathrm{d}t > 0$

$$\sum \nu_B \mu_B < \sum \nu_A \mu_A \qquad \text{(natural process).} \qquad 1.44.7$$

Thus the chemical reaction can in fact take place from left to right only if the inequality (7) holds, and conversely.

If we replace the inequalities by equalities we obtain as the condition for the chemical change in either direction to be a reversible process

$$\sum \nu_A \mu_A = \sum \nu_B \mu_B \qquad \text{(reversible process).} \qquad 1.44.8$$

In other words the condition for equilibrium with respect to the chemical process (5) is

$$\sum \nu_A \mu_A = \sum \nu_B \mu_B \qquad \text{(equilibrium).} \qquad 1.44.9$$

It is convenient for the sake of brevity and elegance to modify our notation relating to chemical changes. We begin by rewriting the chemical reactions quoted at the beginning of this section

$$\begin{aligned}&0=\mathrm{CaO(s)}+\mathrm{CO_2(g)}-\mathrm{CaCO_3(s)}\\&0=2\mathrm{NH_3(g)}-\mathrm{N_2(g)}-3\mathrm{H_2(g)}\\&0=\beta\text{-glucose(aq)}-\alpha\text{-glucose(aq)}\end{aligned}$$

and generally in place of (4) we label the reaction by

$$0=\sum_{\mathrm{B}}\nu_{\mathrm{B}}\mathrm{B} \qquad 1.44.10$$

where ν_{B} has negative values for the species previously denoted by A. Suppose that in a small interval of time $\mathrm{d}t$ the reaction takes place to the extent

$$0=\sum_{\mathrm{B}}\nu_{\mathrm{B}}\,\mathrm{d}\xi\mathrm{B} \qquad 1.44.11$$

then the *reaction rate* is defined by $\mathrm{d}\xi/\mathrm{d}t$. The inequality (3) now becomes

$$\sum_{\mathrm{B}}\nu_{\mathrm{B}}\mu_{\mathrm{B}}\mathrm{d}\xi/\mathrm{d}t<0 \qquad \text{(natural process).} \qquad 1.44.12$$

Thus for the reaction to take place $-\Sigma_{\mathrm{B}}\nu_{\mathrm{B}}\mu_{\mathrm{B}}$ and $\mathrm{d}\xi/\mathrm{d}t$ must have the same sign. The sum $-\Sigma_{\mathrm{B}}\nu_{\mathrm{B}}\mu_{\mathrm{B}}$ is called the *affinity* of the reaction.

It follows immediately that the condition for equilibrium is that the affinity should be zero, that is to say

$$\sum_{\mathrm{B}}\nu_{\mathrm{B}}\mu_{\mathrm{B}}=0 \qquad \text{(equilibrium).} \qquad 1.44.13$$

We may combine the inequality (12) and the equation (13) into the single formula

$$\Big(-\sum_{\mathrm{B}}\nu_{\mathrm{B}}\mu_{\mathrm{B}}\Big)\mathrm{d}\xi/\mathrm{d}t\geqq 0. \qquad 1.44.14$$

The affinity is formally related to the several characteristic functions by

$$\begin{aligned}-\sum_{\mathrm{B}}\nu_{\mathrm{B}}\mu_{\mathrm{B}}&=-(\partial U^{\Sigma}/\partial\xi)_{S^{\Sigma},V^{\Sigma}}=-(\partial H^{\Sigma}/\partial\xi)_{S^{\Sigma},P}\\&=-(\partial \mathcal{A}^{\Sigma}/\partial\xi)_{T,V^{\Sigma}}=-(\partial G^{\Sigma}/\partial\xi)_{T,P}\\&=T(\partial J^{\Sigma}/\partial\xi)_{T,V^{\Sigma}}=T(\partial Y^{\Sigma}/\partial\xi)_{T,P}\\&=T(\partial S^{\Sigma}/\partial\xi)_{U^{\Sigma},V^{\Sigma}}. \qquad 1.44.15\end{aligned}$$

The *affinity* was thus defined by De Donder* in 1922. Of the several equations in formula (15) the most useful and most used is

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* For detailed references see Prigogine and Defay, Chemical Thermodynamics, English translation by Everett, Longmans 1954.

$$-\sum_{\mathrm{B}} \nu_{\mathrm{B}}\mu_{\mathrm{B}} = -(\partial G/\partial \xi)_{T,P}. \qquad 1.44.16$$

The affinity, being a linear combination of chemical potentials, is like the chemical potentials an intensive quantity.

A different and better known notation is that introduced by G. N. Lewis*, namely

$$-\sum_{\mathrm{B}} \nu_{\mathrm{B}}\mu_{\mathrm{B}} = -\Delta G \qquad 1.44.17$$

where the operator Δ denotes increase at constant temperature and constant pressure when ξ increases by unity. Both notations have their advantages and both will be used.

§1.45 *Choice of independent variables*

For practical purposes the most convenient independent variables, other than the composition, to describe any single phase are, usually, temperature and pressure. We shall therefore require to express most thermodynamic properties as functions of T, P and shall be interested in their partial derivatives with respect to T and P. In the case of gases, in contrast to liquids and solids, it is sometimes convenient to choose as independent variables T, V instead of T, P. We shall accordingly also require to express thermodynamic properties as functions of T, V and shall be interested in their partial derivatives with respect to T and V.

§1.46 *Thermal expansivity and isothermal compressibility*

If we regard the volume of a phase of fixed composition as a function of temperature and pressure, we have

$$\mathrm{d}V = (\partial V/\partial T)_P \mathrm{d}T + (\partial V/\partial P)_T \mathrm{d}P. \qquad 1.46.$$

We define α, the *thermal expansivity*, by

$$\alpha = V^{-1}(\partial V/\partial T)_P \qquad 1.46.2$$

and κ_T, the *isothermal compressibility*, by

$$\kappa_T = -V^{-1}(\partial V/\partial P)_T. \qquad 1.46.3$$

Substituting (2) and (3) into (1) we obtain

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* See Lewis and Randall, Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill 1923, p. 226.

$$\mathrm{d}V = \alpha V \mathrm{d}T - \kappa_T V \mathrm{d}P \tag{1.46.4}$$

$$\mathrm{d}\ln V = \alpha \mathrm{d}T - \kappa_T \mathrm{d}P. \tag{1.46.5}$$

Alternatively if we choose to regard P as a function of T, V, we have

$$\mathrm{d}P = \alpha\kappa_T^{-1}\mathrm{d}T - \kappa_T^{-1}V^{-1}\mathrm{d}V. \tag{1.46.6}$$

From (5) we deduce

$$\partial^2 \ln V/\partial T\partial P = (\partial\alpha/\partial P)_T = -(\partial\kappa_T/\partial T)_P. \tag{1.46.7}$$

§1.47 *Maxwell's relations*

For a closed phase α in the absence of chemical reactions we have according to (1.28.7) and (1.28.9)

$$\mathrm{d}\text{Æ}^\alpha = -S^\alpha \mathrm{d}T - P\mathrm{d}V^\alpha \tag{1.47.1}$$

$$\mathrm{d}G^\alpha = -S^\alpha \mathrm{d}T + V^\alpha \mathrm{d}P. \tag{1.47.2}$$

Consequently we have

$$(\partial S^\alpha/\partial V^\alpha)_T = -\partial^2\text{Æ}^\alpha/\partial T\partial V^\alpha = (\partial P/\partial T)_{V^\alpha} = \alpha/\kappa_T \tag{1.47.3}$$

$$(\partial S^\alpha/\partial P)_T = -\partial^2 G/\partial T\partial P = -(\partial V^\alpha/\partial T)_P = -\alpha V^\alpha. \tag{1.47.4}$$

These two relations, due to Maxwell*, are important since they express the dependence of entropy on volume or pressure in terms of the more readily measurable quantities α and κ_T.

§1.48 *Dependence of thermodynamic functions on pressure*

If, as will usually be our choice, we take as independent variables, other than the composition of each phase, the temperature T and the pressure P the relevant characteristic function is the Gibbs function G^α and according to (1.28.9) we have

$$(\partial G^\alpha/\partial P)_T = V^\alpha. \tag{1.48.1}$$

We also have Maxwell's relation (1.47.4)

$$(\partial S^\alpha/\partial P)_T = -\alpha V^\alpha. \tag{1.48.2}$$

Since the enthalpy H^α is related to G^α and S^α by

$$H^\alpha = G^\alpha + TS^\alpha \tag{1.48.3}$$

we have using (1) and (2)

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* Maxwell, Theory of Heat, Longmans 1885 ed. p. 169.

$$(\partial H^\alpha/\partial P)_T=(\partial G^\alpha/\partial P)_T+T(\partial S^\alpha/\partial P)_T=V^\alpha(1-\alpha T). \qquad 1.48.4$$

When we use the independent variables T, P the function U is much less important than G, H. If nevertheless we should require its dependence on the pressure, it is readily derived as follows. By definition

$$U^\alpha=H^\alpha-PV^\alpha \qquad 1.48.5$$

and so by differentiation with respect to P at constant T we obtain

$$(\partial U^\alpha/\partial P)_T=(\partial H^\alpha/\partial P)_T-V^\alpha-P(\partial V^\alpha/\partial P)_T=V^\alpha(\kappa P-\alpha T). \qquad 1.48.6$$

§1.49 *Gibbs–Helmholtz relation*

If, as will usually be our choice, we take as independent variables, other than the composition of each phase, the temperature T and the pressure P we have for the temperature dependence of the relevant characteristic function G^α according to (1.28.9)

$$(\partial G^\alpha/\partial T)_P=-S^\alpha. \qquad 1.49.1$$

If we compare this with the definition of G^α, namely

$$G^\alpha=H^\alpha-TS^\alpha \qquad 1.49.2$$

and eliminate S^α, we obtain

$$H^\alpha=G^\alpha-T(\partial G^\alpha/\partial T)_P. \qquad 1.49.3$$

For a system Σ composed of several phases at the same pressure we obtain from (3) by addition

$$H^\Sigma=G^\Sigma-T(\partial G^\Sigma/\partial T)_P. \qquad 1.49.4$$

If we apply this relation to the final state II and to the initial state I in any isothermal process and take the difference, we obtain

$$\Delta H^\Sigma=\Delta G^\Sigma-T(\partial\Delta G^\Sigma/\partial T)_{P^\mathrm{I},P^\mathrm{II}} \qquad 1.49.5$$

where P^I, P^II denote the initial and final pressures respectively. Formula (5) is known as the *Gibbs–Helmholtz relation.* This name is also sometimes given to formula (4).

By simple transformation we can rewrite these formulae as

$$\{\partial(G^\Sigma/T)/\partial T\}_P=-H^\Sigma/T^2 \qquad 1.49.6$$

$$\{\partial(\Delta G^\Sigma/T)/\partial T\}_{P^\mathrm{I},P^\mathrm{II}}=-\Delta H^\Sigma/T^2 \qquad 1.49.7$$

or alternatively as

$$\{\partial(G^{\Sigma}/T)/\partial(1/T)\}_P = H^{\Sigma} \qquad 1.49.8$$

$$\{\partial(\Delta G^{\Sigma}/T)/\partial(1/T)\}_{P^{\mathrm{I}},P^{\mathrm{II}}} = \Delta H^{\Sigma}. \qquad 1.49.9$$

§1.50 *Dependence of thermodynamic functions on T, V*

As already stated, it is usually convenient to take T, P as independent variables. Only in the case of gases is it sometimes convenient to use instead the independent variables T, V. The dependence of the various thermodynamic functions on these variables is readily obtained and we give the chief results for a phase of fixed composition in the order in which they are conveniently derived without however giving details of the derivations.

$$\mathrm{d}\mathcal{F}^{\alpha} = -S^{\alpha}\mathrm{d}T - P\mathrm{d}V^{\alpha} \qquad 1.50.1$$

$$\mathrm{d}P = \alpha\kappa^{-1}\mathrm{d}T - (\kappa V^{\alpha})^{-1}\mathrm{d}V^{\alpha} \qquad 1.50.2$$

$$\mathrm{d}S^{\alpha} = (\partial S^{\alpha}/\partial T)_V\mathrm{d}T + \alpha\kappa^{-1}\mathrm{d}V^{\alpha} \qquad 1.50.3$$

$$\mathrm{d}U^{\alpha} = T(\partial S^{\alpha}/\partial T)_V\mathrm{d}T + (\alpha T\kappa^{-1} - P)\mathrm{d}V^{\alpha} \qquad 1.50.4$$

$$\mathrm{d}J^{\alpha} = T^{-2}U^{\alpha}\mathrm{d}T + T^{-1}P\mathrm{d}V^{\alpha}. \qquad 1.50.5$$

§1.51 *Use of Jacobians*

Many thermodynamic identities, including those obtained in the preceding sections, can be obtained rapidly and elegantly by the use of Jacobians. The procedures are due to Shaw*, who has shown how to apply them to obtain a tremendous number of identities, some important, others merely amusing. We shall here give a brief sketch of the method, which we shall illustrate by a few simple examples. We would however emphasize that all the simple and most important relations are deduced in this book without using Jacobians, so that the reader not interested in their use may omit this section which does not affect the rest of the book.

We recall that Jacobians are defined by

$$\frac{\partial(x,y)}{\partial(\alpha,\beta)} \equiv -\frac{\partial(y,x)}{\partial(\alpha,\beta)} \equiv \left(\frac{\partial x}{\partial\alpha}\right)_{\beta}\left(\frac{\partial y}{\partial\beta}\right)_{\alpha} - \left(\frac{\partial x}{\partial\beta}\right)_{\alpha}\left(\frac{\partial y}{\partial\alpha}\right)_{\beta} \qquad 1.51.1$$

and that they obey the multiplicative law

$$\frac{\partial(x,y)}{\partial(u,v)}\,\frac{\partial(u,v)}{\partial(\alpha,\beta)} = \frac{\partial(x,y)}{\partial(\alpha,\beta)} \qquad 1.51.2$$

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* Shaw, Phil. Trans. Roy. Soc. London A 1935 **234** 299.

which can be derived by simple geometrical or algebraical considerations on transformation of coordinates.

As particular cases of (1) we have

$$\left(\frac{\partial x}{\partial \alpha}\right)_\beta = \frac{\partial(x, \beta)}{\partial(\alpha, \beta)} = -\frac{\partial(\beta, x)}{\partial(\alpha, \beta)} \tag{1.51.3}$$

$$\left(\frac{\partial y}{\partial \beta}\right)_\alpha = \frac{\partial(\alpha, y)}{\partial(\alpha, \beta)} = -\frac{\partial(y, \alpha)}{\partial(\alpha, \beta)}. \tag{1.51.4}$$

Using (3) and (4) we derive from (2)

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{\partial(x, y)}{\partial(z, y)} = \frac{\partial(x, y)}{\partial(\alpha, \beta)} \bigg/ \frac{\partial(z, y)}{\partial(\alpha, \beta)}. \tag{1.51.5}$$

We now replace α, β by the pair of quantities which we regard as the usually most convenient independent variables, namely the temperature T and the pressure P. We further introduce the following new notation

$$J(x, y) = \frac{\partial(x, y)}{\partial(T, P)} = \left(\frac{\partial x}{\partial T}\right)_P \left(\frac{\partial y}{\partial P}\right)_T - \left(\frac{\partial x}{\partial P}\right)_T \left(\frac{\partial y}{\partial T}\right)_P. \tag{1.51.6}$$

In particular we have

$$\left(\frac{\partial x}{\partial T}\right)_P = J(x, P) = -J(P, x) \tag{1.51.7}$$

$$\left(\frac{\partial x}{\partial P}\right)_T = -J(x, T) = J(T, x). \tag{1.51.8}$$

Using our new notation we have instead of (5)

$$\left(\frac{\partial x}{\partial z}\right)_y = \frac{J(x, y)}{J(z, y)}. \tag{1.51.9}$$

The relations (6) and (9) together enable us to express any quantity of the type $(\partial x/\partial z)_y$ in terms of the partial differential coefficients of x, y, z with respect to T, P.

We shall illustrate by two examples, the first a useful one, the second far fetched. We have

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{J(T, H)}{J(P, H)} = -\frac{(\partial H/\partial P)_T}{(\partial H/\partial T)_P} \tag{1.51.10}$$

a relation which we shall meet again in §3.20 where it is derived more simply.

We now take a more complicated, and less useful, example:

$$\left(\frac{\partial H}{\partial G}\right)_U = \frac{J(H,U)}{J(G,U)} = \frac{(\partial H/\partial T)_P(\partial U/\partial P)_T-(\partial H/\partial P)_T(\partial U/\partial T)_P}{(\partial G/\partial T)_P(\partial U/\partial P)_T-(\partial G/\partial P)_T(\partial U/\partial T)_P}$$

$$= \frac{CV(\kappa P-\alpha T)-V(1-\alpha T)(C-\alpha PV)}{-SV(\kappa P-\alpha T)-V(C-\alpha PV)}$$

$$= \frac{C(\kappa P-\alpha T)-(1-\alpha T)(C-\alpha PV)}{-S(\kappa P-\alpha T)-(C-\alpha PV)} \qquad 1.51.11$$

where we have used formulae (1.48.1), (1.48.4), (1.48.6) and we have denoted $(\partial H/\partial T)_P$ by C.

These illustrative examples by no means exhaust the uses to which Jacobians can be put. The reader who is interested is referred to the original papers by Shaw.

§1.52 *Reversible cycles*

Suppose a system is taken through a complete cycle of states. Then as its final state is identical with its initial state, its entropy must be the same at the end as at the beginning. Thus

$$\Delta S=0 \qquad \text{(any cycle).} \qquad 1.52.1$$

If at all stages the system is in equilibrium, so that no irreversible (natural) change takes place, then

$$\Delta S=\sum_i q_i/T_i \qquad \text{(reversible changes)} \qquad 1.52.2$$

where q_i denotes the heat absorbed at the temperature T_i and the summation extends over all the temperatures through which the system passes. Substituting (2) into (1) we obtain

$$\sum_i q_i/T_i=0 \qquad \text{(reversible cycle).} \qquad 1.52.3$$

Evidently, since T_i is always positive, some of the q_i's must be positive and some negative. It is convenient here to modify our notation so as to distinguish between the positive and negative q_i's. We accordingly replace (3) by

$$\sum_r q_r/T_r=\sum_s Q_s/T_s \qquad \text{(reversible cycle)} \qquad 1.52.4$$

where each q_r is a positive quantity of heat taken in at the temperature T_r and each Q_s is a positive quantity of heat given out at the temperature T_s.

According to the first law of thermodynamics the work $-w$ done by the system during the cycle is given by

$$-w=\sum_i q_i=\sum_r q_r-\sum_s Q_s. \qquad 1.52.5$$

The ratio η defined by

$$\eta=-w/\sum_r q_r=(\sum_r q_r-\sum_s Q_s)/\sum_r q_r=1-\sum_s Q_s/\sum_r q_r \qquad 1.52.6$$

is called by engineers the *thermodynamic efficiency* of the cycle.

Let us suppose that there is a maximum temperature $T_{\max}$ and a minimum temperature $T_{\min}$, between which temperatures the cycle is confined. The following question arises. Subject to this restriction on the temperatures, what is the maximum possible value of η? The answer is obviously obtained by making

$$T_r=T_{\max} \qquad (\text{all } r) \qquad 1.52.7$$

$$T_s=T_{\min} \qquad (\text{all } s). \qquad 1.52.8$$

This means that positive absorption of heat occurs only at the highest temperature $T_{\max}$ and positive loss of heat occurs only at the lowest temperature $T_{\min}$. No heat is exchanged with the surroundings at any temperature intermediate between $T_{\max}$ and $T_{\min}$. In other words the passages from $T_{\max}$ to $T_{\min}$ and the reverse are adiabatic. Thus the cycle consists entirely of isothermal absorption of heat at $T_{\max}$, isothermal emission of heat at $T_{\min}$, and adiabatic changes from $T_{\max}$ to $T_{\min}$ and from $T_{\min}$ to $T_{\max}$. Such a cycle was first considered by Carnot* and is called *Carnot's cycle.*

For Carnot's cycle we have by substituting from (7) and (8) into (4)

$$\sum_r q_r/T_{\max}=\sum_s Q_s/T_{\min} \qquad (\text{Carnot's cycle}). \qquad 1.52.9$$

Now substituting from (9) into (6) we obtain

$$\eta=1-T_{\min}/T_{\max} \qquad (\text{Carnot's cycle}). \qquad 1.52.10$$

There is sometimes confusion between Carnot's cycle and reversible cycles. It will be observed that Carnot's cycle is a very special case of a reversible cycle.

A completely isothermal cycle is a special case of Carnot's cycle. For such a cycle

$$T_{\max}=T_{\min}=T \qquad (\text{isothermal cycle}) \qquad 1.52.11$$

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* Carnot, Réflexions sur la puissance motrice du feu, Bachelier, Paris, 1824. Reprinted in 1912 by Hermann, Paris and in 1953 by Blanchard, Paris, together with some notes discovered after Carnot's death in 1832 and communicated to the Académie des Sciences in 1878 by Carnot's brother.

$$\sum_r q_r = \sum_s Q_s \qquad \text{(isothermal cycle)} \qquad 1.52.12$$

$$w = 0 \qquad \text{(isothermal cycle)} \qquad 1.52.13$$

$$\eta = 0 \qquad \text{(isothermal cycle).} \qquad 1.52.14$$

Formula (13) is known as *Moutier's theorem**.

We shall have no occasion to make any further reference to cycles. They are important in engineering thermodynamics for the treatment of engines and refrigerators, but these fall outside the subject-matter of this book.

§1.53 *Surface phases*

We have hitherto assumed that every system consists of one or more completely homogeneous phases bounded by sharply defined geometrical surfaces. This is an over-simplification, for the interface between any two phases will rather be a thin layer across which the physical properties vary continuously from those of the interior of one phase to those of the interior of the other. We must now consider the thermodynamic properties of these surface layers between two phases. We shall begin by considering a plane interface and shall in §1.60 extend our considerations to a curved interface.

The following treatment is essentially that of van der Waals junior and Bakker†. It is less abstract than the alternative treatment of Gibbs.‡

Figure 1.2 represents two homogeneous bulk phases, α and β, between

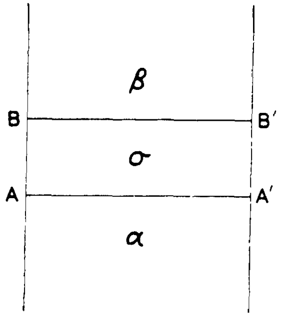

Fig. 1.2. Plane interface between two phases

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* Moutier, Bulletin de la Société philomathique 1875 Aug. 11th.

† Van der Waals and Bakker, Handb. Experimentalphysik, 1928 vol. **6**. See also Verschaffelt, Bull. Acad. Belg. Cl. Sci. 1936 **22** No. 4, pp. 373, 390, 402; Guggenheim, Trans. Faraday Soc. 1940 **36** 398.

‡ Gibbs, Collected Works, Longmans, vol. **1**, p. 219.

which lies the surface layer σ. The boundary between σ and α is the plane AA′, that between σ and β the parallel plane BB′. All properties of σ are uniform in directions parallel to AA′, but not in the direction normal to AA′. At and near AA′ the properties are identical with those of the phase α; at and near BB′ they are identical with those of the phase β. Subject to these conditions there is freedom of choice in placing the planes AA′ and BB′. It will be possible and natural though not essential, so to place the planes AA′ and BB′ that the uniform distance between them is submicroscopic and usually less than 10^{-6} cm, if not less than 10^{-7} cm.

§1.54 *Interfacial tension of plane interface*

Since the surface layer σ is a material system with a well-defined volume and material content, its thermodynamic properties require no special definition. We may speak of its temperature, Helmholtz function, composition, and so on just as for a homogeneous bulk phase. The only functions that call for special comment are the pressure and the interfacial tension. In any homogeneous bulk phase the force across any unit area is equal in all directions and is called the pressure. But in σ the force across unit area is not the same in all directions. If, however, we choose any plane of unit area parallel to AA′ and BB′, then the force normal to it has the same value for all positions of the plane whether it lie in α, β, or σ; this value of the force normal to unit area is called the pressure P. Suppose, on the other hand, we choose a plane perpendicular to AA′ and extending below AA′ and above BB′; let this plane have the form of a rectangle of height h (parallel to AB) and of thickness l (perpendicular to the plane of the paper). Then the force across this plane will be equal to $Phl-\gamma l$, where P is the above-defined pressure and γ is called the *interfacial tension.* If the height of this plane is chosen to extend exactly from AA′ to BB′, then the force across it will be equal to $P\tau l-\gamma l$ if the height AB is denoted by τ. Let the surface layer have an area A and a volume V^{σ} so that

$$V^{\sigma}=\tau A. \tag{1.54.1}$$

Suppose the area to be increased to $A+\mathrm{d}A$, the thickness to $\tau+\mathrm{d}\tau$, and the volume to $V^{\sigma}+\mathrm{d}V^{\sigma}$, the material content remaining unaltered. Then the work done on σ by the forces across AA′ and BB′ is $-PA\,\mathrm{d}\tau$. The work done by the forces parallel to the planes AA′ and BB′ is independent of the shape of the perimeter and for the sake of simplicity we may suppose the perimeter to be a rectangle. The work done by the latter forces is then evidently $-(P\tau-\gamma)\mathrm{d}A$. The total work done on σ is therefore

$$-PA\,\mathrm{d}\tau-(P\tau-\gamma)\mathrm{d}A=-P(A\,\mathrm{d}\tau+\tau\,\mathrm{d}A)+\gamma\,\mathrm{d}A$$
$$=-P\,\mathrm{d}V^{\sigma}+\gamma\,\mathrm{d}A. \qquad 1.54.2$$

This expression takes the place of $-P\,\mathrm{d}V^{\alpha}$ for a homogeneous bulk phase.

§1.55 *Helmholtz function of surface layer*

For the most general variation of the Helmholtz function of a homogeneous bulk phase we have the fundamental equation (1.28.7)

$$\mathrm{d}\mathcal{F}^{\alpha}=-S^{\alpha}\mathrm{d}T-P\,\mathrm{d}V^{\alpha}+\sum_i\mu_i\mathrm{d}n_i^{\alpha}. \qquad 1.55.1$$

For a surface phase σ the dependence of the Helmholtz function on the temperature and the composition will be exactly analogous to that for a bulk phase; this follows directly from the definitions of entropy and chemical potentials. But for its dependence on size and shape we must replace $-P\,\mathrm{d}V^{\alpha}$ by the expression (1.54.2). We thus obtain the formula

$$\mathrm{d}\mathcal{F}^{\sigma}=-S^{\sigma}\mathrm{d}T-P\,\mathrm{d}V^{\sigma}+\gamma\,\mathrm{d}A+\sum_i\mu_i\mathrm{d}n_i^{\sigma}. \qquad 1.55.2$$

There is no need to add superscripts to T, P, μ_i because these must have values uniform throughout α, β, and σ in order that there may be thermal, hydrostatic, and physico-chemical equilibrium.

§1.56 *Integrated relation. Gibbs function of surface phase*

Since equation (1.55.2) is homogeneous of first degree in $\mathcal{F}^{\sigma}$, S^{σ}, V^{σ}, A, and n_i^{σ} it follows by Euler's theorem that

$$\mathcal{F}^{\sigma}+PV^{\sigma}-\gamma A=\sum_i n_i^{\sigma}\mu_i. \qquad 1.56.1$$

This formula is the analogue of

$$\mathcal{F}^{\alpha}+PV^{\alpha}=\sum_i n_i^{\alpha}\mu_i \qquad 1.56.2$$

for a bulk phase.

In analogy with the definition of the Gibbs function G^{α} of a bulk phase

$$G^{\alpha}=U^{\alpha}-TS^{\alpha}+PV^{\alpha}=\mathcal{F}^{\alpha}+PV^{\alpha} \qquad 1.56.3$$

we now define the Gibbs function G^{σ} of the surface phase by

$$G^{\sigma}=U^{\sigma}-TS^{\sigma}+PV^{\sigma}-\gamma A=\mathcal{F}^{\sigma}+PV^{\sigma}-\gamma A \qquad 1.56.4$$

We deduce from (1.55.1) and (4)

$$\mathrm{d}G^{\sigma} = -S^{\sigma}\mathrm{d}T + V^{\sigma}\mathrm{d}P - A\,\mathrm{d}\gamma + \sum_i \mu_i \mathrm{d}n_i^{\sigma} \qquad 1.56.5$$

$$G^{\sigma} = \sum_i n_i^{\sigma}\mu_i. \qquad 1.56.6$$

From time to time papers have been published maintaining that μ_i has a value μ_i^{σ} in the surface differing from its value $\mu_i^{\alpha} = \mu_i^{\beta}$ in the two bulk phases. The worst of these papers are sheer nonsense, the best of them merely confused. In the better papers the quantity denoted by μ_i^{σ} is a different quantity from that denoted by μ_i in the present text which follows Gibbs.

The last two formulae are the analogues of

$$\mathrm{d}G^{\alpha} = -S^{\alpha}\mathrm{d}T + V^{\alpha}\mathrm{d}P + \sum_i \mu_i \mathrm{d}n_i^{\alpha} \qquad 1.56.7$$

$$G^{\alpha} = \sum_i n_i^{\alpha}\mu_i \qquad 1.56.8$$

for a bulk phase α. From the above relations it is evident that, as in a bulk phase, the chemical potential μ_i is equal to the partial Gibbs function defined by $(\partial G/\partial n_i)_{T,P,\gamma,n_j}$.

§1.57 *Analogue of Gibbs–Duhem relation*

If we differentiate (1.56.6) we obtain

$$\mathrm{d}G^{\sigma} = \sum_i \mu_i \mathrm{d}n_i^{\sigma} + \sum_i n_i^{\sigma}\mathrm{d}\mu_i \qquad 1.57.1$$

and subtracting (1.56.5) from this

$$S^{\sigma}\mathrm{d}T - V^{\sigma}\mathrm{d}P + A\,\mathrm{d}\gamma + \sum_i n_i^{\sigma}\mathrm{d}\mu_i = 0 \qquad 1.57.2$$

which is the analogue for a surface phase of the Gibbs–Duhem relation (1.30.2) for a bulk phase.

If we divide (2) throughout by A we obtain the more convenient form;

$$S_A^{\sigma}\mathrm{d}T - \tau\,\mathrm{d}P + \mathrm{d}\gamma + \sum_i \Gamma_i^{\sigma}\mathrm{d}\mu_i = 0 \qquad 1.57.3$$

where S_A^{σ} denotes S^{σ}/A and Γ_i denotes the amount of the species i in unit area of the surface phase σ and is thus defined by

$$\Gamma_i = n_i^{\sigma}/A. \qquad 1.57.4$$

We recall that τ is the thickness of the surface layer, that is to say the length AB in figure 1.2.

§1.58 *Invariance of relations*

We must now study what happens to the several formulae for surface layers if either of the chosen boundaries is moved in a direction normal to itself. We may regard the volume V^{σ} of the surface layer as defined in terms of the volume V^{Σ} of the whole system and the volumes V^{α} and V^{β} of the two bulk phases by the equation

$$V^{\sigma}=V^{\Sigma}-V^{\alpha}-V^{\beta}. \tag{1.58.1}$$

Similarly U^{σ}, S^{σ}, and n_i^{σ} are defined by

$$U^{\sigma}=U^{\Sigma}-U^{\alpha}-U^{\beta} \tag{1.58.2}$$

$$S^{\sigma}=S^{\Sigma}-S^{\alpha}-S^{\beta} \tag{1.58.3}$$

$$n_i^{\sigma}=n_i^{\Sigma}-n_i^{\alpha}-n_i^{\beta}. \tag{1.58.4}$$

If now the geometrical surface AA′ is moved so that V^{α} is decreased by an amount $V^{\alpha}\delta^{\alpha}$ then it is evident that V^{σ} becomes increased by the same amount $V^{\alpha}\delta^{\alpha}$. At the same time U^{σ}, S^{σ}, n_i^{σ} become increased by $U^{\alpha}\delta^{\alpha}$, $S^{\alpha}\delta^{\alpha}$, $n_i^{\alpha}\delta^{\alpha}$. It is readily verified that all the formulae of §1.54 to §1.57 remain unaltered. Exactly the same considerations apply if the geometrical surface BB′ is moved so that V^{β} is decreased by an amount $V^{\beta}\delta^{\beta}$. In particular the value of γA remains invariant and consequently the value of γ remains invariant. We shall see in §1.64 that for a curved surface the value of γ is not invariant.

§1.59 *Gibbs geometrical surface*

We have hitherto postulated that the inhomogeneous layer is completely confined between the geometrical surfaces AA′ and BB′. This restriction may be removed if we accept the possibility that some of the quantities U^{σ}, S^{σ}, n_i^{σ} may become negative. In particular we may make the two surfaces AA′ and BB′ coincide somewhere inside the inhomogeneous layer. This convention defined by

$$V^{\sigma}=0 \tag{1.59.1}$$

was used by Gibbs. It is more elegant but more difficult to visualize than the treatment based on figure 1.2 with $V^{\sigma}>0$. The single geometrical surface is called the *Gibbs geometrical surface.*

According to Gibbs' convention formulae (1.55.2), (1.56.1), (1.56.4), (1.56.5), and (1.56.6) reduce to

$$\mathrm{d}\mathcal{F}^{\sigma} = -S^{\sigma}\mathrm{d}T + \gamma\mathrm{d}A + \sum_i \mu_i \mathrm{d}n_i^{\sigma} \qquad 1.59.2$$

$$U^{\sigma} - TS^{\sigma} - \gamma A = \sum_i n_i^{\sigma}\mu_i \qquad 1.59.3$$

$$G^{\sigma} = U^{\sigma} - TS^{\sigma} - \gamma A \qquad 1.59.4$$

$$\mathrm{d}G^{\sigma} = -S^{\sigma}\mathrm{d}T - A\,\mathrm{d}\gamma + \sum_i \mu_i \mathrm{d}n_i^{\sigma} \qquad 1.59.5$$

$$G^{\sigma} = \sum_i n_i^{\sigma}\mu_i \qquad 1.59.6$$

respectively. These formulae and the value of γ are all invariant with respect to the position of the Gibbs geometrical surface.

In the simplest system, namely a single substance existing as liquid+vapour with a planar boundary, it is convenient to place the Gibbs geometrical surface so that $n^{\sigma}=0$. Formula (2) then reduces to

$$\mathrm{d}\mathcal{F}^{\sigma} = -S\mathrm{d}T + \gamma\mathrm{d}A. \qquad 1.59.7$$

§1.60 *Interfacial tension of curved interface*

We must now consider under what conditions the formulae already derived for plane interfaces may be applied to curved interfaces. We shall see that the formulae strictly derived for plane interfaces may be applied to curved interfaces with an accuracy sufficient for experimental purposes provided that the thickness of the inhomogeneous surface layer is small compared with its radii of curvature*.

For the sake of simplicity let us first consider a system consisting of two homogeneous bulk phases α and β connected by a surface layer σ having the form of a circular cylindrical shell. Figure 1.3 shows a cross-section of the phases α and β separated by the surface layer σ, bounded by the circular cylinders AA′ and BB′ with common axis O. There is complete homogeneity in the direction normal to the diagram. The properties of the surface layer σ are supposed identical at all points the same distance from the axis through O. Throughout the phase α and extending up to AA′ there is a uniform pressure P^{α}; throughout the phase β, and extending down to BB′, there is a uniform pressure P^{β}. Between AA′ and BB′ the pressure P_{r} parallel to the radii of the cylinders AA′ and BB′ varies continuously, but not necessarily monotonically, from the value P^{α} to the value P^{β}.

In the previous discussion of plane surfaces it was pointed out that the geometrical planes AA′ and BB′ may be placed an arbitrary distance apart.

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* Guggenheim, Trans. Faraday Soc. 1940 **36** 397.

For the present discussion of curved surfaces it is on the contrary postulated that the circular cylindrical surfaces AA′ and BB′ should be placed as near together as is consistent with the condition that the inhomogeneous layer be contained between them. According to this condition we may usually expect the distance AB to be about 10^{-7} cm. We shall denote by a distances measured radially from O, and in particular by a_α and a_β, the distances OA and OB respectively.

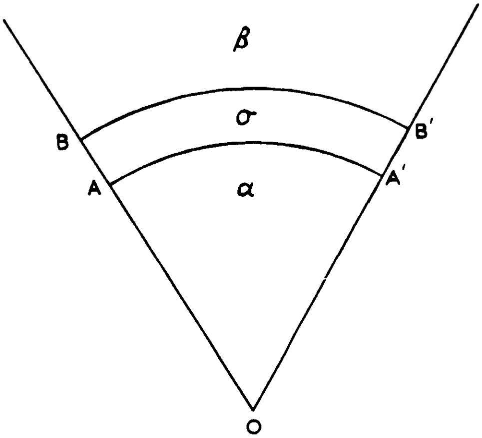

Fig. 1.3. Curved interface between two phases

Whereas the force per unit area across any element of surface inside either homogeneous phase is independent of the orientation of the element (Pascal's law), this is not the case in the inhomogeneous layer σ. It is convenient to denote the force per unit area in the direction parallel to the surface AA′ and BB′ by $P_r - Q$. Both P_r and Q are functions of a. Q is zero at $a = a_\alpha$ and at $a = a_\beta$, but, at least somewhere between, Q is greater than zero. It is conceivable that Q might be negative somewhere between $a = a_\alpha$ and $a = a_\beta$, but its average value in this range is unquestionably positive.

According to elementary statics the mechanical equilibrium of the matter enclosed by AA′B′B requires that for all values of a

$$\mathrm{d}(P_r a) = (P_r - Q)\,\mathrm{d}a \qquad 1.60.1$$

or

$$\mathrm{d}P_r = -(Q/a)\,\mathrm{d}a. \qquad 1.60.2$$

If we integrate (2) from a_β to a_α we obtain

$$P^\alpha - P^\beta = \int_{a_\alpha}^{a_\beta} (Q/a)\,\mathrm{d}a. \qquad 1.60.3$$

We now arbitrarily choose any length $\hat{a}$ subject only to the restriction

$$a_\alpha < \hat{a} < a_\beta \qquad 1.60.4$$

and we define a quantity $\hat{\gamma}$ by

$$\hat{\gamma} = \hat{a} \int_{a_\alpha}^{a_\beta} (Q/a)\mathrm{d}a. \qquad 1.60.5$$

From (3) and (5) we deduce

$$P^\alpha - P^\beta = \hat{\gamma}/\hat{a} \qquad \text{(circular cylinder).} \qquad 1.60.6$$

For the sake of simplicity we have considered an interface with the form of a circular cylinder. For a spherical interface we find by similar reasoning instead of (6)

$$P^\alpha - P^\beta = 2\hat{\gamma}/\hat{a} \qquad \text{(sphere).} \qquad 1.60.7$$

We may call $\hat{\gamma}$ *interfacial tension,* but its exact value depends on the choice of $\hat{a}$. We must now distinguish between the case $a_\beta - a_\alpha \ll a_\alpha$ and the case when this inequality does not hold. In the former case the distinction between a_α, a_β, and $\hat{a}$ is trivial; we may then replace (6) by

$$P^\alpha - P^\beta = \gamma/a \qquad \text{(circular cylinder)} \qquad 1.60.8$$

and (7) by

$$P^\alpha - P^\beta = 2\gamma/a \qquad \text{(sphere).} \qquad 1.60.9$$

For an interface of other shapes the geometry is somewhat more complicated and the general formula obtained is

$$P^\alpha - P^\beta = \gamma/\varrho_1 + \gamma/\varrho_2 \qquad 1.60.10$$

where ϱ_1, ϱ_2 are the principal radii of curvature of the interface. We shall see in §1.62 how formula (9) is the basis for measuring γ. The quantities measured are $P^\alpha - P^\beta$ and a; the value of γ is then calculated by formula (9). In the contrary case when the inequality $a_\beta - a_\alpha \ll a_\alpha$ does not hold γ can neither be uniquely defined nor accurately measured. A mathematical analysis of this situation is given in §1.64.

§1.61 *Pressure within a bubble*

Let us consider a bubble having the form of a thin spherical film of liquid of internal and external radii a_i and a_e. If P^i denotes the pressure nearer to the centre than the film, P^e the pressure further from the centre than the film, and P' the pressure in the liquid film itself, we have, according to (1.60.9)

$$P^{\mathrm{i}}-P'=2\gamma/a_{\mathrm{i}} \qquad 1.61.1$$

$$P'-P^{\mathrm{e}}=2\gamma/a_{\mathrm{e}} \qquad 1.61.2$$

so that

$$P^{\mathrm{i}}-P^{\mathrm{e}}=(2/a_{\mathrm{i}}+2/a_{\mathrm{e}})\gamma \qquad 1.61.3$$

or neglecting the difference between a_{i} and a_{e}

$$P^{\mathrm{i}}-P^{\mathrm{e}}=4\gamma/a. \qquad 1.61.4$$

§1.62 *Determination of interfacial tension*

The commonest method of determining the value of the interfacial tension γ depends on formula (1.60.9). This method is shown diagrammatically in figure 1.4. Two fluid phases α and β are represented, the one shaded the other not shaded. They are separated partly by the plane surfaces AA″ and A′A‴, and partly by the curved surface BB′ in the capillary tube PP′Q′Q of internal radius r. We may, with sufficient accuracy, regard the surface BB′ as a segment of a sphere. Let the centre of this sphere be denoted by O and let θ be the angle between OB and the horizontal OX or alternatively the angle between the tangential plane to BB′ at B and the wall of the vertical capillary tube. Then the radius of curvature of the surface BB′ is $r/\cos\theta$.

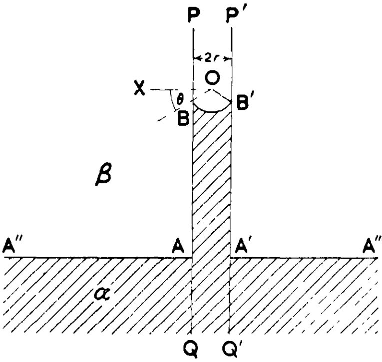

Fig. 1.4. Capillary rise due to interfacial tension

Let P^0 denote the pressure at the plane surfaces AA″ and A′A‴. It will also be the pressure inside the capillary tube at the height AA′. Let the pressures at the height BB′ be denoted by P^α in the phase α and by P^β in the phase β. Then

$$P^\alpha=P^0-\varrho^\alpha gh \qquad 1.62.1$$

$$P^{\beta}=P^{0}-\varrho^{\beta}gh \qquad 1.62.2$$

where ϱ^{α}, ϱ^{β} denote the densities of the phases α and β, g is the acceleration due to gravity, and h is the height AB. But, according to (1.60.9), since the radius of curvature is $r/\cos\theta$

$$P^{\beta}-P^{\alpha}=2\gamma(\cos\theta)/r. \qquad 1.62.3$$

Comparing (1), (2), and (3) we obtain

$$2\gamma(\cos\theta)/r=(\varrho^{\alpha}-\varrho^{\beta})gh. \qquad 1.62.4$$

Thus, from measurement of ϱ^{α}, ϱ^{β}, r, θ, and h we can calculate γ.

In the case that the surface BB′ is concave towards the bottom, its radius of curvature will have the opposite sign, and so h will also have the opposite sign. That is to say, BB′ will lie below AA′.

§1.63 *Independence of interfacial tension of curvature*

Let us now turn to the question whether the interfacial tension depends on the curvatures. We shall see that when the question is precisely defined it answers itself. In asking the question it is not sufficient to state that we vary the curvatures; we require also to state what we keep constant. For the question to be useful it should apply to the actual conditions of the experimental measurement of interfacial tension. For definiteness let us consider the capillary rise method described in the preceding section. The values of the temperature T and the chemical potentials μ_i are uniform throughout the system, and so, whatever be the size and shape of the capillary, these variables have the same values at the curved surface, where the surface tension is measured, as in the bulk phases. Hence to be useful the question should be worded: how does γ depend on ϱ_1, ϱ_2 for given values of T and the μ_i's? According to equation (1.57.3) the variation of γ under these restrictions is given by

$$\mathrm{d}\gamma=\tau\,\mathrm{d}P. \qquad 1.63.1$$

In its present application the ambiguity in the exact meaning of P does not matter, since it can be verified that $(P^{\alpha}-P^{\beta})\tau$ is negligible. If now we consider a curved interface, say in a capillary, in equilibrium with a plane interface and we integrate (1) from the pressure at the plane surface to the pressure at the curved interface (either side of it) we again find that the integral of the right side is always negligible. Consequently γ has effectively the same value for the curved surface as for the plane surface with which it is in equilibrium. This is a statement of a principle usually assumed whenever an interfacial tension is measured. It is experimentally verified by the fact that within the experimental accuracy the same value is found for the interfacial tension when capillaries of different size are used, but this verification can be realized only for capillaries with diameters considerably greater than the lower bound allowed by the theory.

Gibbs summed up this situation in the words 'it will generally be easy to determine the surface tension in terms of the temperature and the chemical potentials of the several component species with considerable accuracy for plane surfaces, and extremely difficult or impossible to determine the fundamental equation more completely'.

§1.64 *Mathematical analysis of curved interface*

We have seen that it is extremely difficult if not impossible to devise any experiment which will determine the dependence of interfacial tension on curvature. This follows from the fact that the thickness of the interface is always extremely small compared with its radius of curvature; if this were not so, the interfacial tension could not be measured at all. The present section is concerned with a more exact mathematical analysis of this situation*. The reader is warned that the physical conclusions are entirely negative.

For the present discussion it is sufficient to consider only a spherical interface and it is convenient to follow Gibbs in describing the properties of the system by means of a single geometrical spherical surface lying inside the interfacial layer and concentric with it. For a chosen geometrical surface of area A the interfacial tension γ is defined by the relation

$$U^{\Sigma}-TS^{\Sigma}-\sum_i \mu_i n_i^{\Sigma}=-P^{\alpha}V^{\alpha}-P^{\beta}V^{\beta}+\gamma A \qquad 1.64.1$$

or by the equivalent relation

$$U^{\Sigma}-TS^{\Sigma}+P^{\beta}V^{\Sigma}-\sum_i \mu_i n_i^{\Sigma}=-(P^{\alpha}-P^{\beta})V^{\alpha}+\gamma A. \qquad 1.64.2$$

Since all the quantities on the left, in particular U^{Σ}, S^{Σ}, V^{Σ}, n_i^{Σ} are invariant with respect to a change in the choice of the Gibbs geometrical surface, it follows that the right side is also invariant. But since a change in the Gibbs geometrical surface involves a change in V^{α} but not in P^{α} nor in P^{β} we may expect it also to change the value of γ. In order to investigate this change we denote the radius of the Gibbs geometrical surface by a. We have

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* Guggenheim, Research 1957 **10** 478.

$$V^\alpha = 4\pi a^3/3 \qquad 1.64.3$$

$$A = 4\pi a^2 \qquad 1.64.4$$

and consequently

$$\gamma a^2 - \tfrac{1}{3}(P^\alpha - P^\beta)a^3 = \text{invariant}. \qquad 1.64.5$$

Differentiating (5) with respect to a we obtain

$$P^\alpha - P^\beta = 2\gamma/a + \mathrm{d}\gamma/\mathrm{d}a. \qquad 1.64.6$$

If we denote by a_t the value of a at which γ has a minimum value γ_t we obtain from (6)

$$P^\alpha - P^\beta = 2\gamma_t/a_t \qquad 1.64.7$$

which is of the same form as if there were a tension located exactly at the Gibbs geometrical surface of radius a_t. This surface is accordingly called the *surface of tension.* Substituting from (7) into (5) we obtain

$$\gamma a^2 - \tfrac{2}{3}\gamma_t a^3/a_t = \tfrac{1}{3}\gamma_t a_t^2 \qquad 1.64.8$$

$$\gamma/\gamma_t = \tfrac{2}{3}a/a_t + \tfrac{1}{3}a_t^2/a^2. \qquad 1.64.9$$

From the form of (9) due to Kondo* it follows that γ_t is indeed a minimum, not a maximum, and that the minimum is unique. Many relations are simplified by choosing the surface of tension as the Gibbs geometrical surface since any term containing $\mathrm{d}\gamma/\mathrm{d}a$ vanishes.

It is convenient for some purposes to define a quantity ε by

$$a^3/a_t^3 = 1 + 3\varepsilon. \qquad 1.64.10$$

It is clear that $\varepsilon \ll 1$ if the thickness of the interface is small compared with its radius of curvature. Using (10) we can rewrite (9) as

$$\begin{aligned} \gamma/\gamma_t &= \tfrac{2}{3}(1+3\varepsilon)^{\frac{1}{3}} + \tfrac{1}{3}(1+3\varepsilon)^{-\frac{2}{3}} \\ &= 1 + \varepsilon^2 + \mathrm{O}(\varepsilon^3) \qquad 1.64.11 \end{aligned}$$

where $\mathrm{O}(\varepsilon^3)$ denotes small terms of order ε^3.

If we denote the amount of the substance i per unit volume in the interiors of the bulk phases α and β by c_i^α and c_i^β respectively, then the surface concentration Γ_i is defined by

$$n_i^\Sigma = c_i^\alpha V^\alpha + c_i^\beta V^\beta + \Gamma_i A. \qquad 1.64.12$$

Since n_i^Σ is of course independent of the choice of the Gibbs geometrical surface it follows that the right hand side of (12) must be invariant. In terms of the radius a this implies

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* Kondo, J. Chem. Phys. 1955 **25** 662.

$$\tfrac{1}{3}(c_i^\alpha - c_i^\beta)a^3 + \Gamma_i a^2 = \text{invariant}. \qquad 1.64.13$$

For a single substance we may drop the subscript i and write

$$\tfrac{1}{3}(c^\alpha - c^\beta)a^3 + \Gamma a^2 = \text{invariant}. \qquad 1.64.14$$

In particular

$$\tfrac{1}{3}(c^\alpha - c^\beta)a^3 + \Gamma a^2 = \tfrac{1}{3}(c^\alpha - c^\beta)a_\mathrm{t}^3 + \Gamma_\mathrm{t} a_\mathrm{t}^2. \qquad 1.64.15$$

We now choose a value of a to make Γ vanish. We indicate this by the subscript $_\mathrm{a}$ and call the Gibbs geometrical surface with this radius the *auxiliary surface*. We have then

$$\Gamma_\mathrm{t} a_\mathrm{t}^2 = \tfrac{1}{3}(c^\alpha - c^\beta)(a_\mathrm{a}^3 - a_\mathrm{t}^3). \qquad 1.64.16$$

It is convenient for some purposes to rewrite (16) as

$$\Gamma_\mathrm{t}/(c^\alpha - c^\beta) = \varepsilon_\mathrm{a} a_\mathrm{t} \qquad 1.64.17$$

where ε_a is defined by

$$a_\mathrm{a}^3/a_\mathrm{t}^3 = 1 + 3\varepsilon_\mathrm{a}. \qquad 1.64.18$$

Thermodynamics alone can predict neither the magnitude of ε_a nor the sign of ε_a nor the dependence of ε_a on a_t. Molecular theory indicates that $|\varepsilon_\mathrm{a}| \ll 1$ if a_t is large compared with molecular dimensions. If we denote by γ_a the value of γ referred to the auxiliary surface, we have according to (11)

$$\begin{aligned} \gamma_\mathrm{a}/\gamma_\mathrm{t} &= \tfrac{2}{3}(1+3\varepsilon_\mathrm{a})^{\frac{1}{3}} + \tfrac{1}{3}(1+3\varepsilon_\mathrm{a})^{-\frac{2}{3}} \\ &= 1 + \varepsilon_\mathrm{a}^2 + \mathrm{O}(\varepsilon_\mathrm{a}^3) \end{aligned} \qquad 1.64.19$$

where $\mathrm{O}(\varepsilon_\mathrm{a}^3)$ denotes small terms of order ε_a^3.

Having defined γ_t uniquely we shall now study how the surface tension between a spherical portion of liquid of a single substance and its surrounding vapour depends on the radius of the sphere or, to be more precise, how γ_t depends on a_t. We have at constant temperature the thermodynamic relations

$$\mathrm{d}\gamma_\mathrm{t} = -\Gamma_\mathrm{t}\,\mathrm{d}\mu \qquad 1.64.20$$

$$\mathrm{d}\mu = \mathrm{d}\mu^\alpha = \mathrm{d}P^\alpha/c^\alpha \qquad 1.64.21$$

$$\mathrm{d}\mu = \mathrm{d}\mu^\beta = \mathrm{d}P^\beta/c^\beta \qquad 1.64.22$$

where c^α and c^β are the concentrations defined by $c = n/V$. From (21) and (22) we deduce using (7)

$$\mathrm{d}\mu = \mathrm{d}(P^\alpha - P^\beta)/(c^\alpha - c^\beta) = \mathrm{d}(2\gamma_\mathrm{t}/a_\mathrm{t})/(c^\alpha - c^\beta) \qquad 1.64.23$$

and substituting this into (20)

$$d\gamma_t = -\Gamma_t(c^\alpha - c^\beta)^{-1} d(2\gamma_t/a_t). \qquad 1.64.24$$

Formula (24) does not really tell us much about the dependence of γ_t on a_t because we have no means of measuring Γ_t. By using (17) we can transform (24) to

$$d\gamma_t = -\varepsilon_a a_t d(2\gamma_t/a_t) \qquad 1.64.25$$

or

$$d \ln \gamma_t / d \ln a_t = 2\varepsilon_a/(1+2\varepsilon_a). \qquad 1.64.26$$

The relation (26) is due to Tolman*. It is elegant but uninformative because ε_a is defined according to (18) in terms of a_a/a_t. As already mentioned thermodynamics tells us nothing about the magnitude or even the sign of ε_a and, as emphasized by Koenig†, we have no means of measuring ε_a. Instead of claiming that (26) tells us anything about $d\gamma_t/da_t$ it would be more realistic to say that if we could measure $d\gamma_t/da_t$, that is to say the dependence of surface tension on curvature, we could then use (26) to calculate ε_a and so a_a/a_t. In fact $d\gamma_t/da_t$ is too small to be experimentally determined and this merely confirms that $|\varepsilon_a| \ll 1$.

The several experimental methods of determining surface tension are all based on the use of an equation formally resembling (7). In fact the experimental value γ_e of the surface tension is calculated from the formula

$$\gamma_e = \tfrac{1}{2}(P^\alpha - P^\beta)a_e \qquad 1.64.27$$

where a_e is the radius of the spherical interface estimated either visually or in the capillary-rise method estimated from the radius of the capillary. The most that can be said about the relation of a_e to a_t is that

$$a_e/a_t = 1 + O(\varepsilon_a). \qquad 1.64.28$$

Consequently the most that can be said about the relation of γ_e to γ_t is

$$\gamma_e/\gamma_t = 1 + O(\varepsilon_a). \qquad 1.64.29$$

§1.65 *Basis of thermodynamic laws*

The *zeroth law* in §1.07, the *first law* in §1.10, and the *second law* in §1.20 have all been quoted as fundamentally independent assumptions. From this point of view their justification is the empirical fact that all conclusions from

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* Tolman, J. Chem. Phys. 1949 **17** 333.

† Koenig, J. Chem. Phys. 1950 **18** 449.

these assumptions are without exception in agreement with the experimentally observed behaviour in nature.

The form in which these laws have been enunciated is essentially that used by Born*. There are other alternative forms; some more, others less abstract, but all of an entirely empirical nature; that is to say that their justification is agreement between their implications on the one hand and experiment on the other.

It is, however, possible to obtain a deeper insight into the fundamental principles from a statistical point of view. It is in fact possible to derive these principles from our knowledge of the structure of matter including the elements of quantum theory together with a single statistical assumption of a very general form. It is a matter of taste whether to choose as a basis several empirical principles which make reference neither to atomic theory nor to quantum theory, or to choose a single principle superposed on atomic theory and quantum theory. The former choice, the one adopted in this book, is the method of *classical thermodynamics*; the latter choice corresponds to the more modern science which we call *statistical thermodynamics.*

There are however other relations of a general nature which follow naturally and directly from the statistical thermodynamic formulation, but which cannot be derived from the zeroth, first, and second laws of classical thermodynamics. The relations to which we refer are of several types concerning respectively

(a) entropy changes in highly disperse systems (i.e. gases);
(b) entropy changes in very cold systems (i.e. when $T \to 0$);
(c) entropy changes associated with mixing of very similar substances (e.g. isotopes).

The three types are of comparable importance. They resemble one another in relating to entropy changes. Their formulation in terms of classical thermodynamics is either complicated or inaccurate or else involves reference to conceptions inherently foreign to classical thermodynamics. As already mentioned they all follow naturally and directly from the statistical thermodynamic formulation.

We shall devote the following chapter to a digression on *statistical thermodynamics*, describing in general terms the methods of this science just sufficiently to give the reader an idea of the source of the relations in question without attempting to derive them in detail. The reader interested in the complete derivations must refer to a standard text-book on *statistical thermodynamics.*

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* Born, Phys. Z. 1921 **22** 218.

§1.66 *Third law*

It has been customary to refer to the three types of general relations mentioned in the preceding section in three quite different ways. The relations of type (a) are referred to as the determination of *entropy constants*, those of type (b) as the *third law* of thermodynamics and those of type (c) merely as the formulae for *entropy of mixing*. This biased discrimination between types of relations of comparable importance and generality is difficult to defend. We accordingly reject this unbalanced terminology and instead choose as our *third law* the following statement.

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 particular one can obtain formulae for entropy changes in highly disperse systems (i.e. gases), for those in very cold systems (i.e. when $T \rightarrow 0$), and for those associated with the mixing of very similar substances (e.g. isotopes).