CHAPTER III

THE SECOND PRINCIPLE OF THERMODYNAMICS

3.1. The Entropy

The first principle of thermodynamics states an energy relation for every process that we may consider. But it does not say anything about whether this process might actually occur at all. It is the second principle that faces this problem and provides at the same time a rigorous criterion to decide when a system is in a state of thermodynamic equilibrium.

Thermodynamic processes may be classified into three categories: natural, impossible or antinatural and reversible.

Natural processes are always in greater or lesser degree, irreversible, and the direction in which they occur is obviously towards equilibrium, by definition of equilibrium. Expansion of a gas into a vacuum, heat conduction through a finite temperature gradient, combination of oxygen and hydrogen at room temperature producing water, diffusion of one gas into another under a finite concentration gradient, freezing of supercooled water – these are examples of natural, irreversible processes. We might imagine the reverse processes: contraction of a gas under no external pressure, heat flowing from one body to another at a higher temperature, etc. But these, as well as other more complicated processes whose absurdity would seem less obvious, are impossible in nature; their impossibility is prescribed by the second principle.

Natural processes may produce opposite changes in a system, depending on the external conditions. We can, in general, reduce the irreversibility of these processes by modifying their paths so that the difference between the actual values of the state variables and the values that would correspond to an equilibrium state is reduced through all the stages of the process. If we continue doing this indefinitely, we tend to a common limit for processes producing either one change or its opposite. This limit is called a reversible process, as we have already seen in Chapter I, Section 8. A reversible process is thus an ideal limit, which cannot actually be realized but to which one can approximate indefinitely, and may be defined as a series of states that differ infinitesimally from equilibrium and succeed each other infinitely slowly, while the variables change in a continuous way. As it may be noticed, we have assumed that, according to experience, the rate of the process tends to zero as the conditions tend to that of equilibrium.

Referring to the previous examples, expansion of a gas with pressure p against an external pressure $p-\mathrm{d}p$, heat conduction along an infinitesimal temperature gradient, etc., are reversible processes. By reversing the sign of the infinitesimal difference from equilibrium conditions (replacing $\mathrm{d}p$ by $-\mathrm{d}p$, $\mathrm{d}T/\mathrm{d}x$ by $-\mathrm{d}T/\mathrm{d}x$, etc.), the reversible process of the opposite sense will occur.

We make now the following statement: for every reversible process there is a positive integrating* factor $1/\tau$ of the differential expression δQ, which is only dependent on the thermal state and which is equal for all thermodynamic systems. A state function S is thus defined (cf. Chapter I, Section 2), the *entropy*, by the exact differential $\mathrm{d}S$:

$$\mathrm{d}S = \left(\frac{\delta Q}{\tau}\right)_{\text{rev}}. \tag{1}$$

We further state that for irreversible processes

$$\mathrm{d}S > \left(\frac{\delta Q}{\tau}\right)_{\text{irr}}. \tag{2}$$

So that for any process we may write

$$\mathrm{d}S \geqslant \left(\frac{\delta Q}{\tau}\right) \tag{3}$$

and the inequality and equality symbols shall always correspond to irreversible and reversible processes, respectively. This formula is the mathematical expression of the second principle of thermodynamics.

It may be shown that τ turns out to be proportional to the absolute ideal gas temperature in all its range of validity, and as the proportionality factor is arbitrary, the simplest choice is to take $\tau = T$. We shall now consider this problem.

3.2. Thermodynamic Scale of Absolute Temperature

Let us first consider a Carnot cycle performed by an ideal gas. The cycle is reversible and consists of two isotherms, at temperatures T_1 and $T_2 < T_1$, and two adiabats (Figure III-1).

Let us compute the work A and the heat Q for the four steps (in the sense indicated by the arrows):

$$\text{(I)} \qquad \Delta U_{\text{I}} = 0; \qquad Q_1 = -A_{\text{I}} = \int_{\text{A}}^{\text{B}} p\,\mathrm{d}V = nR^*T_1 \ln\frac{V_{\text{B}}}{V_{\text{A}}}$$

$$\text{(II)} \qquad Q_{\text{II}} = 0; \qquad -A_{\text{II}} = -\Delta U_{\text{II}} = C_{\text{v}}(T_1 - T_2)$$

$$\text{(III)} \qquad \Delta U_{\text{III}} = 0; \qquad Q_2 = -A_{\text{III}} = -nR^*T_2 \ln\frac{V_{\text{C}}}{V_{\text{D}}}$$

$$\text{(IV)} \qquad Q_{\text{IV}} = 0; \qquad -A_{\text{IV}} = -\Delta U_{\text{IV}} = -C_{\text{v}}(T_1 - T_2).$$

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* It might have been taken negative. This is a matter of convention.

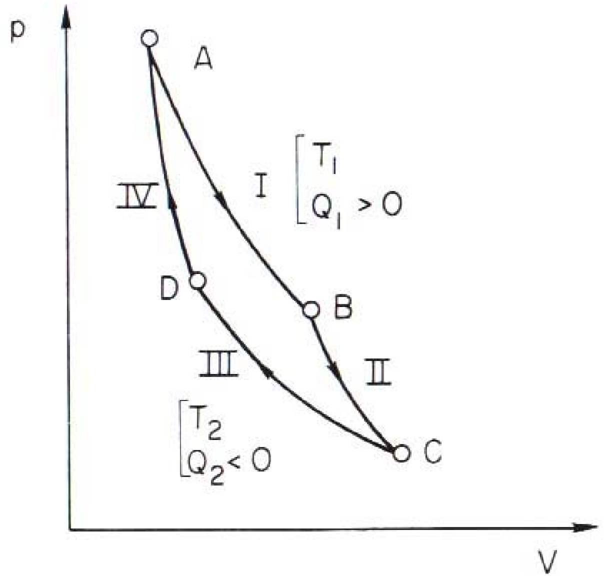

Fig. III-1. Carnot's cycle.

The sum of the four terms ΔU is zero, as it should be for a cycle. The work terms in the two adiabats cancel each other. The gas absorbs the quantity of heat $Q_1 > 0$ from the hotter reservoir and rejects $Q_2 < 0$ to the colder one. Furthermore, from Poisson's relations

$$\frac{T_1}{T_2} = \left(\frac{V_C}{V_B}\right)^{\eta - 1} = \left(\frac{V_D}{V_A}\right)^{\eta - 1}$$

we derive

$$V_B/V_A = V_C/V_D \tag{4}$$

which, introduced in the expressions for Q_1 and Q_2, gives:

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \tag{4}$$

or

$$\frac{|Q_2|}{Q_1} = \frac{T_2}{T_1}. \tag{5}$$

The application of Equation (1) to the same cycle would give, considering that τ must remain constant in each isotherm:

$$\frac{Q_1}{\tau_1} + \frac{Q_2}{\tau_2} = 0 \tag{6}$$

or

$$\frac{|Q_2|}{Q_1} = \frac{\tau_2}{\tau_1}. \tag{7}$$

Therefore, if we write

$$\frac{\tau_2}{\tau_1} = \frac{T_2}{T_1}, \tag{8}$$

Equation (1) is obeyed.

This shows that τ must be taken as proportional to T (absolute ideal gas temperature as defined in Chapter I, Section 5) for the ideal gas of the Carnot cycle.

In order to generalize this result, we should follow the usual procedure by which the mathematical expression of the second principle is shown to derive from physical considerations based on the impossibility of a perpetuum mobile of the second kind (cf. Section 4). As a first step, we should show that Equation (4) is also valid for any reversible cycle performed between two heat sources T_1 and T_2, independently of the nature of the cycle and of the systems (Carnot's theorem), while for an irreversible cycle, $(Q_1/T_1)+(Q_2/T_2)<0$. Finally we might show that any other cycle may be decomposed into, or referred to, a number of Carnot cycles (reversible cycles between two isotherms and two adiabats performed by any fluid), which is made to tend to infinity if the temperature varies continuously for the main cycle. We shall omit here these derivations, for which we refer to any good textbook on general thermodynamics. We shall only quote the final result, which is the formula

$$\oint \frac{\delta Q}{T} \leqslant 0 \tag{9}$$

where the circle in the integral sign indicates that it refers to a cycle and the inequality sign corresponds, as always, to the irreversible case. And, as from Equation (3) it follows that in every case

$$\oint \frac{\delta Q}{\tau} \leqslant 0 \tag{10}$$

we conclude that τ is always proportional, and may be put equal, to T:

$$\tau = T. \tag{11}$$

The equality is achieved by choosing again the value 273.16 K for the reference state, namely the triple point of water. We have now the thermodynamic or Kelvin scale of temperature defined by

$$T = 273.16 \frac{|Q|}{|Q_t|} \tag{12}$$

where Q_t is the heat taken from, or given to, a source in thermal equilibrium with the triple point of water, in a reversible cycle between this source and any other one, to which correspond the values Q and T. As the cycle can be performed, in principle, by any system, this definition of temperature is completely general, covering any possible thermal states, and coincides with the ideal gas absolute temperature for all the range covered by this one.

3.3. Formulations of the Second Principle

We shall, therefore, write the second principle as

$$\mathrm{d}S \geqslant \frac{\delta Q}{T}. \tag{13}$$

The entropy is thus defined (through Equation (13) with the equality sign, for reversible processes) as a state function and, just as in the case of the internal energy, it has an arbitrary additive constant. This constant can be fixed by choosing a reference state for which we write $S=0$. The third principle of thermodynamics provides an absolute reference state (temperature of zero Kelvin for all perfect crystalline solids), but its study, essential in chemical thermodynamics, can be omitted in this book of applications to the atmosphere.

It should be remarked that, as was the case for pressure, the temperature of the system is not defined for irreversible processes. The meaning of T in this case is the temperature of the heat sources in contact with the system.

Other expressions of the second principle for particular cases are:

finite process: $$\Delta S \geqslant \int \frac{\delta Q}{T} \tag{14}$$

adiabatic process: $$\mathrm{d}S \geqslant 0 \tag{15}$$

isentropic process: $$0 \geqslant \delta Q \tag{16}$$

finite isothermal process: $$\Delta S \geqslant \frac{Q}{T} \tag{17}$$

cycle: $$\oint \frac{\delta Q}{T} \leqslant 0. \tag{18}$$

Their derivation from Equation (13) is trivial. Equation (15) tells us that if a process is adiabatic and reversible, it is also isentropic.

If in any process we consider a larger system including the primitive system plus all the bodies with which it exchanged heat, the process becomes adiabatic for the total system and, according to Equation (15), $\mathrm{d}S_{\mathrm{total}} \geqslant 0$. In that sense it is sometimes said, rather loosely, that the entropy 'of the universe' increases in every natural process.

3.4. Lord Kelvin's and Clausius' Statements of the Second Principle

If we consider a system performing a cycle in such a way that at the end it has exchanged heat with only one source T, Equation (18) gives

$$\frac{Q}{T} \leqslant 0$$

and, as $T > 0$, $Q \leqslant 0$. On the other hand, from the first principle it follows that $A = -Q$.

It is, therefore, impossible to construct a cyclic device that will produce work ($A<0$) and no other effect than the cooling of a unique heat source ($Q>0$). This impossibility of a "*perpetuum mobile* of the second kind" is Lord Kelvin's statement of the second principle.

If we now consider a system performing a cycle between two sources T_1 and $T_2<T_1$, without any production or consumption of work, we shall have

$$\frac{Q_1}{T_1}+\frac{Q_2}{T_2}\leqslant 0$$

but by hypothesis and the first law ($A=0$, $Q_1+Q_2=0$), $Q_1=-Q_2=Q$. It follows that $Q=Q_1\geqslant 0$ (and $Q_2\leqslant 0$). Therefore, it is impossible to construct a cyclic device that will produce the sole effect of transferring heat from a colder to a hotter reservoir. This is Clausius' statement of the second principle.

Therefore these two traditional statements, which are alternative bases for the development of the second principle and its applications, appear as immediate consequences of the mathematical formulation in Equation (13).

3.5. Joint Mathematical Expressions of the First and Second Principles. Thermodynamic Potentials

By introducing Equation (13) in the expressions of the first principle (Chapter II, Section 3) we obtain

$$\mathrm{d}U\leqslant T\,\mathrm{d}S+\delta A \tag{19}$$

and for the case in which $\delta A=-p\,\mathrm{d}V$:

$$\mathrm{d}U\leqslant T\,\mathrm{d}S-p\,\mathrm{d}V \tag{20}$$

$$\mathrm{d}H\leqslant T\,\mathrm{d}S+V\,\mathrm{d}p. \tag{21}$$

In the last two expressions, U and H appear as functions of S and V, and S and p, respectively, as independent variables. It is also convenient to have general expressions where the pairs T, V and T, p appear as the independent variables. Two new state functions are defined with that purpose:

$$\text{Helmholtz function or free energy*} \quad = F = U - TS \tag{22}$$

$$\begin{aligned}\text{Gibbs function or free enthalpy*} \quad &= G = H - TS \\ &= U + pV - TS. \end{aligned}\tag{23}$$

Both functions are also called thermodynamic potentials. By differentiating F

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* These are the denominations and symbols recommended internationally. Helmhotz function has also been called *work function* and represented by the letter A. Gibbs function has also been known as the *free energy* and represented by F. Thus Helmholtz function is sometimes referred to as *Helmholtz free energy*, in order to avoid ambiguity.

and introducing it in Equation (20), and by differentiating G and introducing it in Equation (21), two new joint expressions of both thermodynamic principles are obtained:

$$\mathrm{d}F \leqslant -S\,\mathrm{d}T - p\,\mathrm{d}V \tag{24}$$

$$\mathrm{d}G \leqslant -S\,\mathrm{d}T + V\,\mathrm{d}p\,. \tag{25}$$

We shall make use mainly of the last one. In all four Equations (20), (21), (24), (25), the inequality sign holds for irreversible processes (p is then the external pressure exerted upon the system, and T the temperature of the heat sources in contact with it) and the equality sign for reversible processes.

We may summarize these expressions or *fundamental equations* in the following table, where U, H, F and G are considered as the *characteristic functions*:

Characteristic function	Independent variables	Fundamental equation	
U	S, V	$\mathrm{d}U \leqslant T\,\mathrm{d}S - p\,\mathrm{d}V$	(26)
H	S, p	$\mathrm{d}H \leqslant T\,\mathrm{d}S + V\,\mathrm{d}p$	
F	T, V	$\mathrm{d}F \leqslant -S\,\mathrm{d}T - p\,\mathrm{d}V$	
G	T, p	$\mathrm{d}G \leqslant -S\,\mathrm{d}T + V\,\mathrm{d}p$	

We see that these expressions have a helpful symmetry, where the choice of independent variables can be represented schematically by

$$\begin{array}{ccc} U & S & H \\ V & & p \\ F & T & G. \end{array}$$

Each characteristic function is associated with the two adjacent variables. The convenience of these particular associations becomes apparent through the simplicity of many derivations and the equilibrium conditions. It should be noticed, however, that this symmetry only holds under the restriction $\delta A = -p\,\mathrm{d}V$; thus, if this restriction was not imposed, we should substitute Equations (21) and (25) by

$$\mathrm{d}H \leqslant T\,\mathrm{d}S + V\,\mathrm{d}p + p\,\mathrm{d}V + \delta A \tag{27}$$

$$\mathrm{d}G \leqslant -S\,\mathrm{d}T + V\,\mathrm{d}p + p\,\mathrm{d}V + \delta A \tag{28}$$

and the advantages of defining H and G would be lost.

All these thermodynamic functions (U, H, S, F, G) are state functions to which the mathematical concepts reviewed in Chapter II, Section 2 apply. In particular, we can apply Equations (1) and (13) from Chapter II to the differential expressions in

Equations (26). The first ones give:

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p = T$$

$$\left(\frac{\partial F}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial F}{\partial V}\right)_T = -p \tag{29}$$

$$\left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T = V.$$

And applying (Chapter II – Equation (13)), the so-called Maxwell relations are obtained:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V; \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p; \qquad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p. \tag{30}$$

Other relations could also be obtained by combining Equations (29) and (30).

We could write the mathematical expression of the second principle in Equation (13) in the alternative way

$$\mathrm{d}S = \frac{\delta Q}{T} + \frac{\delta Q'}{T} \tag{31}$$

with

$$\delta Q' \geqslant 0. \tag{32}$$

With this definition, the inequality sign in the fundamental Equations (26) could be substituted by the subtraction of $\delta Q'$ from the right hand side; for instance, the first equation would read

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V - \delta Q': \tag{33}$$

$\delta Q'$ is called *Clausius' non-compensated heat*, and gives a measure of the irreversibility of the process.

It should be understood that the set (29) are always true, whether we are considering reversible or irreversible processes (both derivatives and right hand sides are state functions or state variables depending only on the state of the system and not on the path under consideration), but T and p are defined only in a system in conditions of equilibrium. Thus in (26), when the process is irreversible and the inequality sign prevails, T and p represent the temperature of the sources in contact with the system and the external pressure on the system. The conditions of irreversibility are established by the differences between these and the equilibrium values: $(T - T_{\text{eq}})$ (thermal irreversibility), $(p - p_{\text{eq}})$ (mechanical irreversibility). If we equate $\mathrm{d}U$ given by (33) for an irreversible path with the first (26) when applied to the same change by a reversible path, we find

$$\delta Q' = (T - T_{\text{eq}})\,\mathrm{d}S + (p - p_{\text{eq}})\,\mathrm{d}V,$$

which measures the degree of irreversibility for the former process.

3.6. Equilibrium Conditions and the Sense of Natural Processes

Let us consider again the fundamental Equation (20):

$$T\,\mathrm{d}S \geqslant \mathrm{d}U + p\,\mathrm{d}V$$

and let us assume that we have a closed system in a certain state. We may imagine that this system undergoes an infinitesimal change, through an arbitrarily chosen process. We call this a *virtual* change, and the process that produces it may in principle be a natural, impossible or reversible one. To find out which is the case, we calculate the variations $\mathrm{D}S$, $\mathrm{D}U$ and $\mathrm{D}V$ (where the differential symbol D rather than d indicates that the variation is a virtual and not a real one) and we try the previous equation with these values. If we obtain

$$T\,\mathrm{D}S > \mathrm{D}U + p\,\mathrm{D}V$$

the process is a natural or spontaneous one. If an equality sign holds, the imagined process is a reversible one. If the inequality is of an opposite sense, the process is impossible.

It should be remarked that, although the process investigated may turn out to be of any kind (reversible, natural or impossible), the actual calculation of virtual variations of some of the state functions will require consideration of reversible paths.

We may now repeat this procedure with every process that we can imagine. If none of them are natural (if in every case we obtain signs $\leqslant$), the system is in thermodynamic equilibrium, as all virtual processes turn out to be either impossible or reversible. It may happen that for some of these processes signs $\leqslant$ are obtained, while for others we find $>$; the system is then in equilibrium with respect to the former, but not to the latter ones. This would be the case, for instance, of ice at a temperature above 0 °C and of water below 0 °C; we may have, in both cases, thermal and mechanical equilibrium, but not chemical equilibrium, as the change of physical state will be a spontaneous process. The ice will actually be melting; the water may remain indefinitely liquid, but this is a *metastable* equilibrium (cf. Chapter 1, Section 4).

It will be convenient, in general, to apply one or another of Equations (26), imposing *restrictive conditions* to the virtual processes (e.g., that they occur at constant temperature and pressure). By so doing, we obtain particularly simple conditions (e.g., for constant T and p, we should have $\mathrm{D}G \geqslant 0$ for every virtual process, if the system is in equilibrium). These are summarized below :

General equation:	$T\,\mathrm{d}S \geqslant \delta Q$ or any of Equations (26)				
Restrictive conditions:	Adiabatic process $\delta Q = 0$	Isentropic process $\mathrm{d}S = 0$		Isothermal process $\mathrm{d}T = 0$	
		Isochoric $\mathrm{d}V = 0$	Isobaric $\mathrm{d}p = 0$	Isochoric $\mathrm{d}V = 0$	Isobaric $\mathrm{d}p = 0$
Resulting equation:	$\mathrm{d}S \geqslant 0$	$\mathrm{d}U \leqslant 0$ (from 20)	$\mathrm{d}H \leqslant 0$ (from 21)	$\mathrm{d}F \leqslant 0$ (from 24)	$\mathrm{d}G \leqslant 0$ (from 25)
Equilibrium criterion:	$\mathrm{D}S \leqslant 0$	$\mathrm{D}U \geqslant 0$	$\mathrm{D}H \geqslant 0$	$\mathrm{D}F \geqslant 0$	$\mathrm{D}G \geqslant 0$

Thus an important use of the thermodynamic potentials, whose differentials are expressed in terms of the differentials of T, p, V, is to obtain simple criteria for the natural sense of processes and of thermodynamic equilibrium, convenient for practical application.

The equations in the table tell us that, if a system is in equilibrium, the function S is a maximum with respect to any adiabatic change, and that the functions U, H, F, G are minima with respect to isentropic isochoric, isentropic isobaric, isothermal isochoric and isothermal isobaric changes, respectively. There also becomes apparent the convenience of associating U with S, V, etc.

A simple example will serve to illustrate these ideas. Let us consider a system consisting of water in the presence of water vapor at pressure p, and let the virtual process be the condensation of an infinitesimal number n of moles of vapor. It will be convenient to use the Gibbs function G. In order to calculate $\mathrm{D}G$, we must perform the virtual change along a reversible path; this can be the isothermal compression of n moles of vapor from p to the equilibrium pressure p_s (saturated vapor pressure), and then condensation at constant T and p_s. In the first step we have:

$$\mathrm{D}_1 G = n \int_{p}^{p_s} V\,\mathrm{d}p = n \int_{p}^{p_s} R^* T\,\mathrm{d}\ln p = n R^* T \ln \frac{p_s}{p}.$$

During the second step, $\mathrm{D}_2 G = 0$, because both T and p_s remain constant. We then bring back the condensed n moles to the original pressure p. This contributes a term

$$\mathrm{D}_3 G = n \int_{p}^{p_s} V_w\,\mathrm{d}p \cong n V_w (p - p_s),$$

(where V_w is the molar volume of water) which has opposite sign to the previous term D_1G but is much smaller, because $V_w \ll V$ (molar volume of vapor); in fact it is quite negligible. Therefore*:

$$DG = D_1G + D_3G > 0 \quad \text{if } p < p_s$$

$$DG = D_1G + D_3G < 0 \quad \text{if } p > p_s.$$

In the first case, the process is impossible; in the second one, it is spontaneous. If we reverse the virtual process, the opposite will be true. We can conclude that only if $p_s = p$ (for which $DG = 0$ in both cases) can there be equilibrium. We can also conclude that no other equilibrium vapor pressure exists, because only for $p = p_s$ can DG vanish (reversible process).

3.7. Calculation of Entropy

In order to have an expression for $\mathrm{d}S$ with coefficients depending on directly measurable properties, so that we may integrate it to obtain values for finite differences ΔS, we start by expressing $\mathrm{d}S$ as a function of T and p as independent variables:

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial S}{\partial p}\right)_T \mathrm{d}p. \tag{34}$$

This may be compared with the joint expression for both principles that uses enthalpy (Equation (21)):

$$\mathrm{d}S = \frac{1}{T}\,\mathrm{d}H - \frac{V}{T}\,\mathrm{d}p \tag{35}$$

and developing $\mathrm{d}H$ as a function of T and p:

$$\mathrm{d}S = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \frac{1}{T}\left[\left(\frac{\partial H}{\partial p}\right)_T - V\right]\mathrm{d}p. \tag{36}$$

Comparison of the coefficients of $\mathrm{d}T$ in Equations (34) and (36) shows ($\mathrm{d}T$ and $\mathrm{d}p$ being independent, we may compare for $\mathrm{d}p = 0$):

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p = \frac{C_p}{T} \tag{37}$$

(cf. Chapter II, Section 4).

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* This can be demonstrated simply in the critical case of p_s approximately equal to p, for which D_1G becomes, on expansion of the natural logarithm,

$$D_1G = nR^*T\ln(p_s/p) = nVp\ln\left(1 + \frac{p_s - p}{p}\right)$$

$$= nV\{(p_s - p) + \ldots\}.$$

Hence

$$DG = n(p_s - p)(V - V_w) + \ldots$$

The variation of S with p at constant T is given by one of Maxwell's relations (Equations (30)):

$$\left(\frac{\partial S}{\partial p}\right)_{\mathrm{T}} = -\left(\frac{\partial V}{\partial T}\right)_{\mathrm{p}}. \tag{38}$$

This derivative is directly measurable, and is usually expressed as the isobaric expansion coefficient $(1/V)(\partial V/\partial T)_{\mathrm{p}} = \alpha_{\mathrm{p}}$.

We have thus the expression

$$\mathrm{d}S = \frac{C_{\mathrm{p}}}{T}\,\mathrm{d}T - \left(\frac{\partial V}{\partial T}\right)_{\mathrm{p}} \mathrm{d}p = C_{\mathrm{p}}\,\mathrm{d}\ln T - V\alpha_{\mathrm{p}}\,\mathrm{d}p \tag{39}$$

that can be applied conveniently to the computation of entropy changes. A similar expression can be derived as a function of T and V, by introducing U instead of H (therefore using Equation (20) rather than (21)) and following a similar derivation. This gives

$$\mathrm{d}S = \frac{C_{\mathrm{v}}}{T}\,\mathrm{d}T + \left(\frac{\partial p}{\partial T}\right)_{\mathrm{v}} \mathrm{d}V = C_{\mathrm{v}}\,\mathrm{d}\ln T + p\alpha_{\mathrm{v}}\,\mathrm{d}V \tag{40}$$

where $\alpha_{\mathrm{v}} = (1/\mathrm{p})(\partial p/\partial T)_{\mathrm{v}}$ is the isochoric coefficient of pressure rise with temperature.

Equations (39) and (40) permit, by integration from experimental data, the direct calculation of the entropy changes associated with changes in the state of a homogeneous system of constant chemical composition, when no changes in the physical state (fusion, vaporization, sublimation) take place. When the latter changes occur the variation in the entropy is easily calculated; if the change of phase occurs reversibly, the pressure and the temperature are constant during the process (as will be discussed in the next chapter) and $\Delta H = L$. Therefore the entropy changes by

$$\Delta S = \frac{\Delta H}{T} = \frac{L}{T} \tag{41}$$

(for 1 mol). By using both (39), or (40), and (41) the entropy of a substance can be referred to any appropriate reference state.

3.8. Thermodynamic Equations of State. Calculation of Internal Energy and Enthalpy

By comparing the coefficients of $\mathrm{d}p$ in Equations (34) and (36), and introducing Equation (38), we see that

$$\left(\frac{\partial H}{\partial p}\right)_{\mathrm{T}} = V - T\left(\frac{\partial V}{\partial T}\right)_{\mathrm{p}} = V(1 - T\alpha_{\mathrm{p}}). \tag{42}$$

By using U instead of H, and T, V instead of T, p, a similar derivation gives

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p = p(T\alpha_v - 1). \tag{43}$$

Equations (42) and (43) are called the *thermodynamic equations of state*. They solve a problem remaining from Chapter II, Section 5: that of calculating the variations in U and H for processes in which V and p vary. Thus by writing the total differentials

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V \tag{44}$$

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T + \left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p \tag{45}$$

and introducing Chapter II, Equations (29) and (30) and Equations (42) and (43), we obtain

$$\mathrm{d}U = C_v\,\mathrm{d}T + p(T\alpha_v - 1)\,\mathrm{d}V \tag{46}$$

$$\mathrm{d}H = C_p\,\mathrm{d}T + V(1 - T\alpha_p)\,\mathrm{d}p \tag{47}$$

The integration of these formulas completely solves the problem of integrating internal energy and enthalpy for processes without changes of phase. Obviously, the last terms in both (46) and (47) vanish for ideal gases.

If changes of phase occur at constant pressure and temperature, the change in enthalpy, per mole, is given directly by

$$\Delta H = L \tag{48}$$

and that of internal energy, by

$$\Delta U = \Delta H - p\,\Delta V = L - p\,\Delta V \tag{49}$$

The last term in (49) will be negligible for fusion, because the molar volumes of condensed phases are small. For vaporization and sublimation, $\Delta V \cong V_v$ = molar volume of the vapor, and if the vapor is approximated by an ideal gas,

$$\Delta U = L - R^*T \tag{50}$$

By the use of formulas (46) to (50), the internal energy and the enthalpy of a substance can be referred to any appropriate reference state.

3.9. Thermodynamic Functions of Ideal Gases

Either by introducing the gas law into Equation (39), which is general for any system, or by starting from $\mathrm{d}S = \delta Q/T$ and substituting for δQ the expressions of the first principle for ideal gases (Chapter II, Equations (39) and (40)), we derive for ideal gases

$$\begin{aligned} \mathrm{d}S &= C_{\mathrm{p}}\,\mathrm{d}\ln T - R^*\,\mathrm{d}\ln p \\ &= C_{\mathrm{v}}\,\mathrm{d}\ln T + R^*\,\mathrm{d}\ln V \\ &= C_{\mathrm{v}}\,\mathrm{d}\ln p + C_{\mathrm{p}}\,\mathrm{d}\ln V \end{aligned} \tag{51}$$

where we have used the relation $\mathrm{d}\ln T = \mathrm{d}\ln p + \mathrm{d}\ln V$ (logarithmic differentiation of the gas law).

Integration gives:

$$\begin{aligned} S &= C_{\mathrm{p}}\ln T - R^*\ln p + b \\ &= C_{\mathrm{v}}\ln T + R^*\ln V + b' \\ &= C_{\mathrm{v}}\ln p + C_{\mathrm{p}}\ln V + b''. \end{aligned} \tag{52}$$

And by using the gas law and the relation $C_{\mathrm{p}} - C_{\mathrm{v}} = R^*$ it is easily seen that $b' = b - R^*\ln R^*$ and $b'' = b - C_{\mathrm{p}}\ln R^*$.

With the definition of potential temperature (Chapter II, Equation (55)), we have

$$\mathrm{d}\ln\theta = \mathrm{d}\ln T - \varkappa\,\mathrm{d}\ln p \tag{53}$$

and for the entropy

$$\mathrm{d}S = C_{\mathrm{p}}\,\mathrm{d}\ln\theta. \tag{54}$$

Taking C_{p} as constant, θ may be thus considered as an alternative variable for entropy in reversible processes.

Having now the expressions of U, H (Chapter II, Equations (37) and (38)) and S for ideal gases, those for F and G can immediately be written down. For instance, we have for G:

$$G = (C_{\mathrm{p}}T - C_{\mathrm{p}}T\ln T - bT) + R^*T\ln p + a \tag{55}$$

as a function of T and p, where the terms dependent on T alone are between brackets and a is the additive constant for H.

3.10. Entropy of Mixing for Ideal Gases

Let us assume that we have a mixture of two ideal gases, with partial pressures p_1 and p_2, at temperature T and occupying a volume V. We want to know what difference of entropy exists between this state and that in which the two gases are separate, at their corresponding partial pressures. In order to calculate ΔS, we must link both states by a reversible process; this is done by performing the mixture with the ideal experiment illustrated in Figure III-2. Two cylinders of equal volume V contain initially the two gases; both cylinders have a semipermeable membrane at one end and can be inserted one into the other, as indicated in the figure (the wall's thickness is neglected). A (fixed to cylinder 2) is a semipermeable membrane only permeable to gas 1, and B (fixed to cylinder 1) is a semipermeable membrane only permeable to

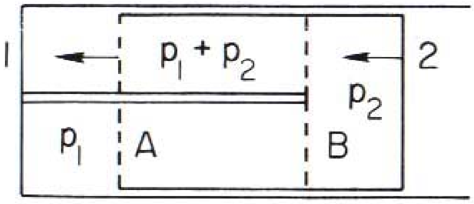

Fig. III-2. Isentropic mixing of ideal gases.

gas 2. As the gas that diffuses freely through each membrane does not exert any pressure on it, the device is in equilibrium and the mixture can be performed reversibly (using an infinitesimal excess of pressure on the external bases until both cylinders enclose the same volume) and isothermally. Neither gas performs any work, and their internal energies remain constant (as the temperature remains constant). Therefore, according to the first principle the process is also adiabatic and, being reversible. isentropic. We conclude that $\Delta S=0$. We can say that the entropy of the mixture is equal to the sum of the *partial entropies*, defined as the entropies of the gases at their partial pressures, when pure and occupying the same volume at the same temperature. This conclusion can obviously be extended to any number of gases, and is known as Gibbs' theorem.

The process of mixing just described must not be confused with that of two gases at the same pressure mixing by diffusion into each other, with a final volume equal to the sum of the two partial volumes. This is an irreversible process, with a finite increase in total entropy.

3.11. Difference Between Heat Capacities at Constant Pressure and at Constant Volume

In Chapter II, Section 5, we found that $C_p - C_v = R^*$ for ideal gases. With the results of the previous sections, we are now in a position to derive the general expression of $C_p - C_v$ for any homogeneous system of constant composition.

The following well-known relation between partial derivatives can be readily obtained

$$\left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_V . \tag{56}$$

From Chapter II, Equations (29) and (30) we see that the last term of Equation (56) is C_v, and that we can write for C_p, considering that $H = U + pV$,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p . \tag{57}$$

Solving for $(\partial U/\partial T)_p$ in Equation (57), introducing this expression into Equation (56) and rearranging we obtain:

$$C_p - C_v = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p. \tag{58}$$

By a similar procedure, using H instead of U, we can also obtain the expression

$$C_p - C_v = \left[V - \left(\frac{\partial H}{\partial p}\right)_T\right]\left(\frac{\partial p}{\partial T}\right)_V. \tag{59}$$

Introducing now Equation (43) into (58), we obtain

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_p = TpV\alpha_v\alpha_p. \tag{60}$$

The coefficients α_v, α_p are small for condensed phases (solid or liquid), and therefore the difference $C_p - C_v$ is usually (but not always) small, and can be neglected in a first approximation.

We can express the calculated difference using the coefficient of compressibility $k = -(1/V)(\partial V/\partial p)_T$ instead of α_V. We apply the following relation between partial derivatives

$$\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_p = \frac{(\partial V/\partial p)_T(\partial p/\partial T)_V}{(\partial V/\partial T)_p} = -1 \tag{61}$$

which gives

$$\frac{\alpha_p}{\alpha_v k} = p \tag{62}$$

so that Equation (60) can also be written

$$C_p - C_v = \frac{TV\alpha_p^2}{k}. \tag{63}$$

These formulas refer the difference $C_p - C_v$ to quantities that are directly measurable.

Application of Equation (63) to *water* gives

$$C_p - C_v = 0.13\,\text{cal mol}^{-1}\,\text{K}^{-1} \text{ at } 0\,°\text{C}$$

$$= 0\ \ \text{cal mol}^{-1}\,\text{K}^{-1} \text{ at } 4\,°\text{C}$$

(temperature of density maximum)

$$= 0.18\,\text{cal mol}^{-1}\,\text{K}^{-1} \text{ at } 25\,°\text{C}$$

to be compared with

$$C_p = 18.02\,\text{cal mol}^{-1}\,\text{K}^{-1}.$$

Therefore, in most problems the difference can be neglected with sufficient approximation. This is not always the case for liquids; for instance, for *ethyl ether*

$$C_p - C_v = 11\ \text{cal mol}^{-1}\,\text{K}^{-1}$$

to be compared with

$$C_p = 40 \text{ cal mol}^{-1}\text{K}^{-1}; \qquad C_v = 29 \text{ cal mol}^{-1}\text{K}^{-1}.$$

We shall only be concerned with water and ice, for which the approximation $C_p \cong C_v$ is valid.

The specific heat capacities of water c_w and ice c_i are

$$\begin{array}{rll} c_w = 1.00 & \text{cal g}^{-1}\text{K}^{-1} = 4.18 \times 10^3 \text{ J kg}^{-1}\text{K}^{-1} \text{ at} & 40\,^\circ\text{C} \\ 1.01 & \text{cal g}^{-1}\text{K}^{-1} = 4.22 \times 10^3 \text{ J kg}^{-1}\text{K}^{-1} \text{ at} & 0\,^\circ\text{C} \\ 1.14 & \text{cal g}^{-1}\text{K}^{-1} = 4.77 \times 10^3 \text{ J kg}^{-1}\text{K}^{-1} \text{ at} & -40\,^\circ\text{C} \\ c_i = 0.504 & \text{cal g}^{-1}\text{K}^{-1} = 2.11 \times 10^3 \text{ J kg}^{-1}\text{K}^{-1} \text{ at} & 0\,^\circ\text{C} \\ 0.43 & \text{cal g}^{-1}\text{K}^{-1} = 1.81 \times 10^3 \text{ J kg}^{-1}\text{K}^{-1} \text{ at} & -40\,^\circ\text{C} \end{array}$$

PROBLEMS

1. One mole of ideal gas occupied 10 l at 300 K. It then expands into a vacuum until its volume is 20 l. Calculate the change in entropy and in the Gibbs function.
2. Calculate ΔS (where it is possible) and $\delta Q/T$ for the four processes mentioned in problem Chapter II, Section I, all resulting in the same isothermal compression of an ideal gas.
3. 0.01 kg of supercooled water at $-10\,^\circ$C is observed to freeze. The latent heat of fusion is lost to the surroundings and the ice regains the previous temperature. Calculate ΔU, ΔH, ΔS and ΔG. Neglect the volume variations and the effect of pressure changes in condensed phases and show that within this approximation, $l_s = l_v + l_f$ at the temperature stated. Under what conditions is this strictly true?
4. Assume that only work of compression can be done on a system. What criteria can be derived from the second principle to decide if the system is in equilibrium with respect to (a) adiabatic changes, (b) isothermal changes, (c) isothermal isobaric changes?
5. In problem 5 from Chapter II the effect of pressure change was neglected. Compute now what is the effect of increasing the pressure from $e_{w,0}$ to $e_{w,20}$ (saturation vapor pressures at 0 and 20 °C) on the internal energy and on the enthalpy of 1 g of water at 0 °C. Compare these values with those of problem 5 from Chapter II. The cubic expansion coefficient of water at constant pressure is $-6 \times 10^{-5}\,\text{K}^{-1}$ at 0 °C.
6. Compute the variation in specific enthalpy and in specific entropy of liquid water at 0 °C
   (a) when the pressure is decreased from 1 atm to 0.5 atm.
   (b) when the temperature is decreased to $-10\,^\circ$C (the water remaining liquid).
   Coefficient of cubic expansion of water at 0 °C and constant pressure:
   $\alpha_p = -6 \times 10^{-5}\,\text{K}^{-1}$.

7. How will the air pressure change, if the entropy decreases by 10 J kg^{-1} K^{-1} and the air temperature increases by 2%?
8. In what direction (increase or decrease) does the enthalpy of a system vary when undergoing an irreversible isentropic and isobaric process?
9. 1 kg of dry air at 300 K and 1000 mb is brought to 235 K and a pressure p.
   (a) Knowing that the specific entropy increased by 100 J kg^{-1} K^{-1}, derive the value of p.
   (b) What is the final potential temperature Θ_2?
10. Supercooled water droplets in a cloud freeze. After a while, they have recovered the initial temperature. The pressure did not change. Is the difference of free enthalpy (Gibbs' free energy) between the initial and final states zero, positive or negative? Explain.
11. 1 g of water at 0 °C is cooled to -10 °C, then freezes (the latent heat of freezing being rapidly removed by ventilation during the process) and the ice is finally brought back to 0 °C. Is the total entropy change equal to (i) $-l_{\mathrm{f},-10}/263.15$? (ii) to $(c_{\mathrm{i}} - c_{\mathrm{w}}) \ln \dfrac{273.15}{263.15} - l_{\mathrm{f},-10}/263.15$? (iii) to $-l_{\mathrm{f},0}/273.15$? (c_{i}, c_{w} = specific heat capacities of ice and water, per gram; $l_{\mathrm{f},-10}$, $l_{\mathrm{f},0}$ = latent heat of freezing at -10 °C and at 0 °C, per gram.) Explain.