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NEW FUNDAMENTAL CONCEPTS AND RESULTS IN THERMODYNAMICS WITH CHEMICAL APPLICATIONS

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A thermodynamics of open systems has been developed which provides an entirely new theoretical framework based on novel concepts without any recourse to statistical mechanics. The standard chemical potential is replaced by a convective potential itself derived from a new concept referred to as the "thermobaric potential". Entropy convected by addition of masses into an open system is obtained using only classical concepts without leading to Gibbs' paradox. A generalized Gibbs–Duhem theorem is derived. Application to chemical systems leads to new expressions for the affinity and an "intrinsic" heat of reaction which excludes the heat of mixing and is more representative of the true chemical energy. These expressions involve only mechanical and calorimetric concepts. They are much more general than the standard formulas which are restricted to temperature variations. The van't Hoff–le Chatelier principle is extended to open systems in terms of the new convective potential.

1. Introduction

The thermodynamics of open systems following Gibbs' transitional approach has always been the source of difficulties. Basically this is due to the fact that masses are *added* to the system while the classical definition of energy and entropy are defined as *increases* of these quantities for *given* masses. Gibbs' paradox provides a typical example of inherent inconsistencies. The difficulties are generally resolved by the use of statistical concepts.

However it is possible to develop a new approach to the thermodynamics of open systems which is completely self-consistent and avoids the aforementioned difficulties. This can be accomplished entirely within the framework of classical thermodynamics without introducing any statistical concepts.

The principle of the method is to use a closed physical system of given masses constituted by primary cells and a series of supply cells each containing a pure substance. We also adjoin a large isothermal reservoir at constant temperature called a *thermal well.* The two types of cells and the thermal well constitute a *hypersystem.* Each primary cells is at its own temperature and together they constitute a nonisothermal system.

In any transformation by a *reversible* process the work accomplished on the hypersystem defines the *collective potential.* No external matter or heat is added to the hypersystem and as a consequence it is shown that the collective potential is a function of the state variables of the primary cells only.

Matter is transferred *internally* from the supply cells to the primary cells by a reversible process which we have called a *thermobaric transfer.* This leads to two new concepts, the *thermobaric potential* and the *convective potential*, derived earlier [1] in a less detailed presentation. The key to the procedure of thermobaric transfer is the use of reversible mechanical pumps and heat pumps on the material *within* the hypersystem. While the primary cells are open, the hypersystem is both closed and adiabatic.

The new concept of convective potential replaces Gibbs' chemical potential and is defined for a given hypersystem without any undetermined constant. The basic difference with Gibbs' approach and standard potentials is discussed in detail in section 8.

One of the important features of the new approach is an expression for the entropy *convected* by masses added to the system which avoids Gibbs' paradox. The Gibbs–Duhem theorem is also generalized in terms of the new convective potential. Very general conditions of equilibrium and stability of heterogeneous systems are readily obtained.

Application to chemical reactions leads to new and completely general formulas for the *affinity* and *heat of reaction* already obtained earlier [1] by a slightly different reasoning. They are expressed in terms of purely mechanical and calorimetric concepts. They involve a new *intrinsic heat of reaction* which excludes the heat of mixing and is more representative of the chemical energy than the standard concept. By contrast classical formulas for the affinity and heat of reaction are less general and restricted to temperature variations.

Classical results for reacting perfect gasses are derived very simply from the foregoing general results. A generalized van't Hoff–le Chatelier principle is also derived for an open system in terms of the convective potential.

2. Collective potential of a closed cell

We consider an homogeneous cell at a uniform temperature T which will be called a *primary cell* C_P. We adjoin a large isothermal reservoir at a uniform temperature T_0 referred to as a *thermal well* TW. It is assumed large enough so that a finite quantity of heat added to it changes its temperature only by a negligible amount. The system constituted by the cell C_P and the thermal well TW is called the *hypersystem* (fig. 1).

We assume that this hypersystem undergoes a *reversible transformation.* In this transformation no heat is exchanged between the hypersystem and the environment. However within the system heat may be absorbed by the primary cell and the thermal well by using *reversible heat pumps.* Work is also performed on the system by external forces applied to the primary cell and by the heat pumps. Starting from a given initial state we define the *collective potential* of the system as

$$\mathcal{V} = \mathcal{W}_{PR} + \mathcal{W}_{H} , \tag{2.1}$$

where $\mathcal{W}_{PR}$ is the reversible work on the primary cell and $\mathcal{W}_H$ the work of the heat pumps. Thus $\mathcal{V}$ is equal to the total reversible work done on the system. In this transformation the temperature T of the primary cell may vary.

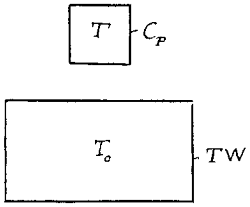

Fig. 1. Hypersystem constituted by a primary cell C_P at temperature T and a thermal well TW at temperature T_0.

Since $\mathcal{V}$ represents the energy of the hypersystem the first principle of thermodynamics yields

$$\mathcal{V} = \mathcal{U}(q_i) + H . \tag{2.2}$$

The quantity $\mathcal{U}$ is the classical energy of C_P. It is a function of the state variables q_i of C_p. The quantity H is the amount of heat energy absorbed by the thermal well. The collective potential $\mathcal{V}$ is thus a function of the state variables q_i and H of the hypersystem.

The important property here is that $\mathcal{V}$ is actually a function of q_i only. This is a consequence of the second principle of thermodynamics and can be shown as follows. Consider an infinitesimal heat pump cycle where dh is the heat energy absorbed at the temperature T by C_P, and dH is the heat absorbed by the thermal well at the temperature T_0. It follows from the second principle (see ref. [2] p. 146) that we may write

$$\mathrm{d}H = -(T_0/T)\,\mathrm{d}h = -T_0\,\mathrm{d}\mathcal{S} , \tag{2.3}$$

where d$\mathcal{S}$ is the increase of entropy of C_p. Hence eq. (2.2) may be written

$$\mathcal{V} = \mathcal{U} - T_0\,\mathcal{S} . \tag{2.4}$$

Since $\mathcal{S}$ is a function of q_i the collective potential

$$\mathcal{V} = \mathcal{V}(q_i) \tag{2.5}$$

is a function only of the state variables q_i of the primary cell C_p. As a consequence we may refer to $\mathcal{V}$ *as the collective potential of the primary cell,* or more simply, as *the cell potential.*

As pointed out [1] the heat pumping need not be accomplished by means of a material cycle. *Black body radiation* may be used. A certain amount of radiation energy extracted from the thermal well is compressed adiabatically to the temperature of the primary cell and injected into it.

If the primary cell undergoes an irreversible transformation without acquiring any heat energy, the first principle yields

$$\mathcal{U} = \mathcal{W}_P , \tag{2.6}$$

where $\mathcal{W}_P$ is the work accomplished on the primary cell in the irreversible transformation. Substitution of eqs. (2.6) in eq. (2.4) yields

$$\mathcal{V} - \mathcal{W}_P = -T_0 \mathcal{S} \, . \tag{2.7}$$

Since no heat is provided to C_P

$$\mathcal{S} \geqslant 0 \tag{2.8}$$

represents the entropy produced and

$$\mathcal{W}_P \geqslant \mathcal{V} \, . \tag{2.9}$$

Hence $\mathcal{V}$ is the minimum work required for a given transformation.

In differential form we may write eq. (2.1) as

$$\mathrm{d}\mathcal{V} = \mathrm{d}\mathcal{W}_{PR} + \mathrm{d}\mathcal{W}_H \, . \tag{2.10}$$

On the other hand the work performed reversibly by the heat pump to inject an amount dh of heat energy into the primary cell is

$$\mathrm{d}\mathcal{W}_H = \mathrm{d}H + \mathrm{d}h \, . \tag{2.11}$$

According to eq. (2.3) we may write

$$\mathrm{d}\mathcal{W}_H = (\theta/T)\, \mathrm{d}h = \theta \, \mathrm{d}\mathcal{S} \, . \tag{2.12}$$

Hence eq. (2.10) becomes

$$\mathrm{d}\mathcal{V} = \mathrm{d}\mathcal{W}_{PR} + \theta \, \mathrm{d}\mathcal{S} \, , \tag{2.13}$$

where

$$\theta = T - T_0 \tag{2.14}$$

is the *excess temperature* and d$\mathcal{S}$ is the *entropy supplied* reversibly to the primary cell by conduction.

The collective potential as a new thermodynamic potential to replace the traditional approach was introduced by the author in 1955 [3] for the purpose of developing a thermodynamics of complex nonisothermal irreversible systems. Although presented at the time in the context of linearity it is obviously quite general. The definition of this potential in the following sections in terms of reversible work on a complex hypersystem including supply cells is a new development [1].

Prior to 1955 an expression similar to eq. (2.4) containing an additional term had been used by Gibbs ([4] p. 40) not as a potential but in an inequality which yields a stability criterion for a system surrounded by an environment at constant pressure and temperature. It was later interpreted as a measure of available energy balance.

3. Collective potential of an open cell. Thermobaric potential

We shall now define and evaluate the collective potential for an open primary cell when masses may be added to the cell. We consider a hypersystem constituted by the primary cell C_P, a thermal well TW and a set of supply cells C_{Sk}, each containing a pure chemical species identified by the index k (fig. 2). The supply cells are large rigid cells all at the same pressure p_0 and the same temperature T_0. For convenience this temperature is chosen to be the same as that of the thermal well but this is not required. However the pressures and temperatures of the supply cells must be chosen the same. As will be shown below (section 5) this condition is required in order to avoid Gibbs' paradox. The material added to the primary cell is provided entirely by the supply cells so that matter is transferred only internally within the hypersystem by reversible work. The supply cells are large enough so that removal of a finite quantity of substance changes the pressure and temperature of the cell by a negligible amount.

We define the collective potential of this hypersystem as in the preceding section. It is the total reversible work accomplished on the hypersystem by forces external to it while no heat energy is exchanged by the hypersystem with the environment. The condition of reversibility requires that in general the work accomplished by the external forces includes the work of heat pumps. The heat acquired or lost by the cells and the thermal well at different temperatures is provided entirely by heat pumps. Arbitrary amounts of the pure substances are also transferred internally and reversibly between C_P and C_{Sk} by a combination of mechanical work accomplished directly by forces applied to the pure substance and by heat pumps.

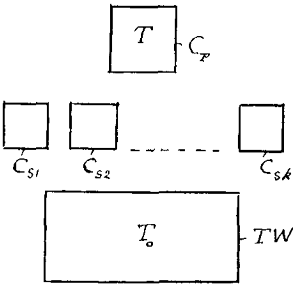

Fig. 2. Hypersystem constituted by a primary cell Cp a set of supply cells C_{Sk} and a thermal well TW.

The collective potential thus defined is expressed in the same form (2.2) as before

$$\mathcal{V} = \mathcal{U} + H\,, \tag{3.1}$$

where H is the heat energy acquired by the thermal well. However $\mathcal{U}$ is now the *collective energy* of the system $C_P + \Sigma_k C_{Sk}$ constituted by the primary cell and set of supply cells. These quantities are defined by their increase above an initial state for which they are assigned the value zero. The state variable of the primary cell C_P are represented by a set q_i plus an additional number of variables m_k each representing the mass of the pure substance k added to the primary cell. On the other hand the state variables of the supply cells are simply the same variables m_k since the masses added to the primary cells are extracted entirely from the supply cells.

As an important consequence the system $C_P + \Sigma_k C_{Sk}$ of primary and supply cells is determined entirely by the state variables of the primary cell. Hence the collective energy $\mathcal{U}$ of the system $C_P + \Sigma_k C_{Sk}$

$$\mathcal{U} = \mathcal{U}(q_i, m_k)\,, \tag{3.2}$$

is a function of the state variables q_i and m_k of the primary cell C_P.

Furthermore it is easy to show that H in expression (3.1) is also a function of q_i and m_k. This is done by following the same procedure as in the preceding section. Taking into account the fact that the transformation is reversible, the total change of entropy of the hypersystem is zero. Hence

$$\mathcal{S} + H/T_0 = 0\,, \tag{3.3}$$

where H/T_0 is the entropy increase of the thermal well and $\mathcal{S}$ the *entropy increase* of the system $C_P + \Sigma_k C_{Sk}$ of primary and supply cells. This entropy is a function of q_i and m_k

$$\mathcal{S} = \mathcal{S}(q_i, m_k)\,. \tag{3.4}$$

Because $\mathcal{U}$ and $\mathcal{S}$ are defined completely by the state of C_P alone we may refer to them as the *collective energy and entropy* of the primary cell. Combining eqs. (3.1), (3.2), (3.3) and (3.4) we derive

$$\mathcal{V} = \mathcal{U}(q_i, m_k) - T_0\,\mathcal{S}(q_i, m_k)\,. \tag{3.5}$$

This important result expresses the fact that the collective potential $\mathcal{V}$ *is a function only of the state variables* $q_i m_k$ *of the primary cell.* Hence again we may refer to $\mathcal{V}$ as the *collective potential of the primary cell* or more simply as the *cell potential.*

We shall now proceed to evaluate $\mathcal{V}$ in terms of measurable quantities. By definition

$$\mathrm{d}\mathcal{V} = \mathrm{d}\mathcal{W}_{\mathrm{PR}} + \sum_k \psi_k \mathrm{d}m_k + \theta\,\mathrm{d}s_{\mathrm{T}}\,. \tag{3.6}$$

The term $\mathrm{d}\mathcal{W}_{\mathrm{PR}}$ is the reversible work of external forces on the primary cell and is the same as in eq. (2.13). The term $\theta\,\mathrm{d}s_{\mathrm{T}}$ as in eq. (2.13) represents the work of a heat pump. We use the notation $\mathrm{d}s_{\mathrm{T}}$ instead of $\mathrm{d}\mathcal{S}$ to indicate that $\mathrm{d}s_{\mathrm{T}}$ is not the total entropy supplied to the cell but only that part which is supplied directly by thermal condution. This distinction is necessary since we shall see that the total collective entropy increase $\mathrm{d}\mathcal{S}$ in the case of an open cell is the result of *both thermal conduction* and *material convection.*

If we put $\mathrm{d}\mathcal{W}_{\mathrm{PR}} = \mathrm{d}s_{\mathrm{T}} = 0$, hence if the primary cell is in a rigid envelope and if no heat is supplied directly to the cell, the remaining terms

$$\mathrm{d}\mathcal{V} = \sum_k \psi_k\,\mathrm{d}m_k \tag{3.7}$$

represent the work required to transfer reversibly masses $\mathrm{d}m_k$ from the supply cells to the primary cell. The quantity ψ_k is the work required to transfer a unit mass of substance k under the conditions described. Since $\mathcal{V}$ depends only on the final state, ψ_k is independent of the path followed in this transfer. We have referred to ψ_k as the *thermobaric potential* of the substance and the corresponding process as a thermobaric transfer [1]. The thermobaric potential may be written

$$\psi_k = \psi_k^{(1)} + \psi_{(1)k}^{(2)} + \psi_k^{(2)}\,. \tag{3.8}$$

The term $\psi_k^{(1)}$ is the work required to extract reversibly a unit mass from the supply cell C_{Sk}. After extraction this mass is now outside C_{Sk} in a state 1 at the temperature T_0 and in thermodynamic equilibrium with C_{Sk}. The unit mass is then brought reversibly to a state 2 at the temperature T of the primary cell and in thermodynamic equilibrium with it. The work required to bring the unit mass from state 1 to state 2 is denoted by $\psi_{(1)k}^{(2)}$. It includes the work $\mathcal{W}_{(1)k}^{(2)}$ of the forces applied directly to the unit mass in combination with the work done by a continuous sequence of reversible heat pumping. We write

$$\psi^{(2)}_{(1)k} = \mathcal{W}^{(2)}_{(1)k} + \int_1^2 \theta \, \mathrm{d}\bar{s}_k \, . \tag{3.9}$$

The second term is the work of heat pumping. The differential $\mathrm{d}\bar{s}_k$ plays the same role as $\mathrm{d}s_\mathrm{T}$ in eq. (3.6). It represents the increase of entropy of a unit mass of substance k due to the absorption of heat provided by the heat pump at each infinitesimal step in the thermobaric transfer.

When the unit mass has been brought to state 2 at the temperature T in thermodynamic equilibrium with the primary cell we inject the mass into this cell by reversible work. This work is represented by the terms $\psi^{(2)}_k$.

The foregoing results are quite general and are valid for solids and fluids. We shall evaluate the thermobaric potential for the case where the *pure substances are fluids* throughout the range of temperature and pressures considered. In this case

$$\psi^{(1)}_k = -p_0/\rho_{0k} \, , \tag{3.10}$$

where ρ_0 is the density of the substance at the temperature T_0 and pressure p_0 of the supply cell. Note that $1/\rho_{0k}$ represents the volume of the unit mass. Similarly we write

$$\psi^{(2)}_k = p_k/\rho_k \, , \tag{3.11}$$

where ρ_k and p_k are respectively the density and pressure of the substance at the temperature T and in equilibrium with the primary cell. The pressure is therefore that of the substance in equilibrium with the contents of the primary cell through a *semipermeable membrane.*

The work performed by the pressure acting on the unit mass of fluid from state 1 to state 2 is

$$\mathcal{W}^{(2)}_{(1)k} = -\int_1^2 p_k \, \mathrm{d}(1/\rho_k) \, . \tag{3.12}$$

Note that $\mathrm{d}(1/\rho_k)$ is the volume differential of the unit mass. Substitution of eqs. (3.9), (3.10), (3.11) and (3.12) into eq. (3.8) and integration by parts of eq. (3.12) yields

$$\psi_k = \int_1^2 ((1/\rho_k) \, \mathrm{d}p_k + \theta \, \mathrm{d}\bar{s}_k) \, . \tag{3.13}$$

This may be written

$$\psi_k = \int_{p_0 T_0}^{p_k T} ((1/\rho_k) \, \mathrm{d}p_k + \theta \, \mathrm{d}s_\mathrm{T}) \, , \tag{3.14}$$

indicating explicitly the initial and final states by p_0, T_0 and p_k, T. To avoid undue heaviness of notation we use the same symbols p_k and T as in the final states for the variable values of pressure and density along the path of integration. As already pointed out the value of ψ_k is independent of the path followed. Eq. (3.14) for ψ_k was derived previously by the author [1].

In the present development we shall restrict ourselves to the case where the pure substances involved are fluids and the primary cell is constituted by a fluid mixture. The cell potential

$$\mathcal{V} = \mathcal{V}(v, T, m_k) \tag{3.15}$$

is then a function of the state variables v, T, m_k of the primary cell where v denotes its volume. The variables v and T play the role of q_i in eqs. (3.2), (3.4) and (3.5). If p denotes the pressure of the fluid mixture in the primary cell we may write the value of $\mathrm{d}\mathcal{W}_\mathrm{PR}$ in eq. (3.6) as

$$\mathrm{d}\mathcal{W}_\mathrm{PR} = -p \, \mathrm{d}v \, . \tag{3.16}$$

Hence eq. (3.6) becomes

$$\mathrm{d}\mathcal{V} = -p \, \mathrm{d}v + \sum_k \psi_k \, \mathrm{d}m_k + \theta \, \mathrm{d}s_\mathrm{T} \, . \tag{3.17}$$

To evaluate $\mathcal{V}$ as a function of v, m_k and T by integrating (3.17) we note that the result is independent of the path of integration. Hence we first integrate at constant volume ($\mathrm{d}v = 0$) and at constant temperature $T_0(\theta = 0)$ and vary the masses injected from zero to m_k. The value of $\mathcal{V}$ obtained is

$$\mathcal{V}^\mathrm{I}(m_k) = \int_0^{m_k} \sum_k \psi_k \, \mathrm{d}m_k \, , \tag{3.18}$$

where

$$\psi_k = \int_{p_0 T_0}^{p_k T_0} (1/\rho_k) \, \mathrm{d}p_k \, . \tag{3.19}$$

We then maintain m_k constant ($\mathrm{d}m_k = 0$) and the same constant temperature $T_0(\theta = 0)$ while varying the volume. During this process $\mathcal{V}$ varies by an amount of

$$\mathcal{V}^{\mathrm{II}}(v, m_k) = -\int_0^v p \, \mathrm{d}v \,, \tag{3.20}$$

where

$$p = p(v, m_k) \tag{3.21}$$

is a function of the volume v at constant temperature T_0 and constant m_k. Finally we maintain constant the volume v ($\mathrm{d}v = 0$) and m_k ($\mathrm{d}m_k = 0$) and vary the temperature of the primary cell. The corresponding variation of $\mathcal{V}$ is

$$\mathcal{V}^{\mathrm{III}}(v, m_k, T) = \int_{T_0}^{T} \theta \, \mathrm{d}s_{\mathrm{T}} = \int_{T_0}^{T} (\theta/T) \, c \, \mathrm{d}T \,, \tag{3.22}$$

where

$$c = c(v, m_k, T) \tag{3.23}$$

is the heat capacity of the primary cell at constant volume v and constant m_k as a function of the temperature. The total value of $\mathcal{V}$ thus obtained is

$$\mathcal{V}(v, m_k, T) = \mathcal{V}^{\mathrm{I}} + \mathcal{V}^{\mathrm{II}} + \mathcal{V}^{\mathrm{III}} \,. \tag{3.24}$$

It is interesting to point out that s_{T} in expression (3.17) is *not a state variable* since it does not represent a total entropy change and excludes the part of entropy change due to material convection $\mathrm{d}m_k$ into the cell. It will be shown below how to express $\mathrm{d}\mathcal{V}$ so that all the differentials are state variables.

Definition of partial pressure: The pressure p_k of the pure substance in thermodynamic equilibrium with the primary cell may be referred to as the *partial pressure* of the substance in the cell. This is purely a *matter of definition* which has the advantage of completely general applicability.

Case of a solid cell: The case where the primary cell is composed of solid matter with pure substances in solid solution or contained in pores has been discussed in a concurrent paper [5].

4. Collective entropy and convective potential

Attention will now be called to an important concept involved in the present analysis, namely the collective entropy (3.4). Assuming a fluid primary cell, v and T play the role of q_i and eq. (3.4) may be written

$$\mathcal{S} = \mathcal{S}(v, m_k, T) \,. \tag{4.1}$$

This collective entropy $\mathcal{S}$ is defined as the increase of entropy of the collection of cells $\mathrm{C_P} + \Sigma_k \mathrm{C}_{\mathrm{S}k}$ constituted by the primary cell and the set of supply cells. As already pointed out this collective entropy $\mathcal{S}$ is a function of the state variables v, m_k and T of the primary cell. This is due to the fact that the state of the supply cells is determined entirely by the masses m_k extracted which are exactly equal to the masses injected into $\mathrm{C_P}$.

We may therefore speak of the *collective entropy of the primary cell.*

Similarly we may speak of the *collective energy (3.2) of the primary cell.* In the present case with q_i represented by v and T we may write this collective energy as

$$\mathcal{U} = \mathcal{U}(v, m_k, T) \,. \tag{4.2}$$

Let us now examine the increase of collective entropy during a thermobaric transfer. There is no change of entropy during extraction of $\mathrm{d}m_k$ from the supply cell since the process is reversible and adiabatic. The mass $\mathrm{d}m_k$ extracted is now in state 1 at the pressure and temperature p_0, T_0. During the process of bringing this mass to state 2 an amount of heat $\mathrm{d}h$ provided by the heat pump is injected into the mass $\mathrm{d}m_k$ at every step. The temperature at each step is denoted by T. During a continuous sequence of steps the entropy of the mass $\mathrm{d}m_k$ is increased by the amount

$$\int_1^2 T^{-1} \mathrm{d}h = \mathrm{d}m_k \int_1^2 \mathrm{d}\bar{s}_k \,, \tag{4.3}$$

where $\mathrm{d}\bar{s}_k$ is the *increase of entropy of a unit mass of the pure substance* k at every step. We may put

$$\int_1^2 \mathrm{d}\bar{s}_k = \bar{s}_k \tag{4.4}$$

and call it the *specific relative entropy of substance* k *in state 2.* Hence eq. (4.3) becomes

$$\int_1^2 T^{-1} \mathrm{d}h = \bar{s}_k \, \mathrm{d}m_k \,. \tag{4.5}$$

This is the increase of collective entropy of the system constituted by the cells $C_P + C_{Sk}$ and the mass dm_k when the latter has been brought to state 2.

The mass dm_k in state 2 is now by definition in thermodynamic equilibrium with the primary cell. Therefore its injection by a reversible process into the primary cell does not change the collective entropy. Hence the increase of collective entropy $d\mathcal{S}$ due to the thermobaric transfer of a mass dm_k is

$$d\mathcal{S} = \bar{s}_k \, dm_k \, . \tag{4.6}$$

When more than one substance is injected into the primary cell the increase of collective entropy is

$$d\mathcal{S} = \sum_k \bar{s}_k \, dm_k \, . \tag{4.7}$$

Note that injection of the masses dm_k is accomplished adiabatically. If we now inject an amount of heat dh_T directly into the primary cell the collective entropy increase due to this heat injection is

$$ds_T = T^{-1} dh_T \, , \tag{4.8}$$

where T is now the temperature of the primary cell. Again dh_T is assumed to be provided by a heat pump. The total increase of collective entropy due to the injection of the masses dm_k and the heat dh_T is the sum of expressions (4.7) and (4.8) namely

$$d\mathcal{S} = \sum_k \bar{s}_k \, dm_k + ds_T \, . \tag{4.9}$$

Using the same notation as in eq. (3.14) for states 1 and 2 we may write the value (4.4) of $\bar{s}_k$ in state 2 as

$$\bar{s}_k = \int_{p_0 T_0}^{p_k T} d\bar{s}_k \, , \tag{4.10}$$

where p_k and T are the pressure and temperature of the pure substance in equilibrium with the primary cell.

With these results we may introduce the collective entropy differential $d\mathcal{S}$ into the value (3.17) of $d\mathcal{V}$. From (4.9) we derive

$$ds_T = d\mathcal{S} - \sum_k \bar{s}_k \, dm_k \, . \tag{4.11}$$

Substitution of this value into eq. (3.17) yields

$$d\mathcal{V} = -p \, dv + \sum_k \phi_k \, dm_k + \theta \, d\mathcal{S} \, , \tag{4.12}$$

where

$$\phi_k = \psi_k - \theta \bar{s}_k \, . \tag{4.13}$$

This result is the same as obtained previously [1] and we shall refer to ϕ_k as the *convective potential.* Because of relation (4.1) we see that the collective entropy $\mathcal{S}$ may replace T as a state variable. Hence with v, m_k and $\mathcal{S}$ as state variables of the primary cell

$$\mathcal{V} = \mathcal{V}(v, m_k, \mathcal{S}) \tag{4.14}$$

becomes a function of these variables. The exact differential (4.12) implies the following fundamental relations

$$(\partial\mathcal{V}/\partial v)_{m_k,\mathcal{S}} = -p \, , \qquad (\partial\mathcal{V}/\partial m_k)_{v,\mathcal{S}} = \phi_k \, ,$$

$$(\partial\mathcal{V}/\partial\mathcal{S})_{v,m_k} = \theta \, . \tag{4.15}$$

They are the same as the relations obtained earlier [1]. The convective potential ϕ_k plays a role similar to a chemical potential μ_k while being different from it. It seems therefore preferable to use a different terminology for ϕ_k instead of considering it as a new definition of μ_k as done in ref. [1]. We should note that ϕ_k in contrast with the standard procedures for μ_k is defined in a precise way by eq. (4.13) and not by eqs. (4.15). The latter constitutes an independent theorem.

By substituting the value (3.14) of ψ_k into eq. (4.13) and taking the differential of ϕ_k we obtain

$$d\phi_k = (1/\rho_k) \, dp_k - \bar{s}_k \, dT \, . \tag{4.16}$$

This can be seen to be the Gibbs function of the pure substance per unit mass except that in contrast with the standard definition *the entropy $\bar{s}_k$ does not contain any undetermined constant.*

As a consequence of eq. (4.16) ϕ_k remains constant through a phase change at constant pressure and temperature.

5. Heat and entropy of mixing and avoidance of Gibbs' paradox

When masses dm_k are injected reversibly we have seen that the change of collective entropy is given by eq. (4.9). If the process is adiabatic

$$ds_T = 0 \, . \tag{5.1}$$

quently the heat of mixing vanishes for perfect gasses

$$h^k_{pT} = 0 \,. \tag{5.12}$$

Hence the entropy produced (5.8) becomes

$$\mathrm{d}s^* = \sum_k \left[\bar{s}_k(p_k, T) - \bar{s}_k(p, T)\right] \mathrm{d}m_k \,. \tag{5.13}$$

The relative entropy of a unit mass of perfect gas is

$$\bar{s}_k(p, T) = \mathcal{M}_k^{-1}\left[\int_{T_0}^{T} c_{kp}(T)\, T^{-1}\mathrm{d}T - R\log(p/p_0)\right], \tag{5.14}$$

where c_{kp} is the molar specific heat at constant pressure, $\mathcal{M}_k$ is the molecular weight, and R is the universal molar gas constant. Substitution of the entropy (5.14) into (5.13) yields

$$\mathrm{d}s^* = R \sum_k \mathcal{M}_k^{-1} \log(p/p_k)\, \mathrm{d}m_k \,. \tag{5.15}$$

In this expression p is the total pressure of the mixture in the primary cell while p_k is the pressure of a pure gas component in equilibrium with the mixture through a semipermeable membrane.

We may express $\mathrm{d}s^*$ by introducing the molar fraction γ_k of each gas in the mixture. The standard notation is avoided here to prevent confusion with cartesian coordinates x_i used below. For a perfect gas mixture we may write

$$p_k = p\gamma_k \,. \tag{5.16}$$

Hence

$$\mathrm{d}s^* = -R \sum_k \mathcal{M}_k^{-1} \log\gamma_k\, \mathrm{d}m_k \,. \tag{5.17}$$

If we apply this to two identical gasses in equal concentrations $\gamma_1 = \gamma_2 = \frac{1}{2}$ and with the same molecular weight $\mathcal{M}_1 = \mathcal{M}_2 = \mathcal{M}$ we find

$$\mathrm{d}s^* = R\mathcal{M}^{-1} \log 2\, \mathrm{d}m \,, \tag{5.18}$$

where $\mathrm{d}m$ is the total mass of gas added ($\mathrm{d}m = \mathrm{d}m_1 + \mathrm{d}m_2$). Hence in this case eq. (5.17) implies that the mixture of identical gasses by diffusion under conditions of constant pressure and temperature leads to an increase in entropy. The fallacy of course lies in the assumption of the validity of eq. (5.16) in this case. Since p_k is defined by equilibrium through a semipermeable membrane application of eq. (5.16) to identical gasses implies that the membrane can act as a Maxwell demon and distinguish between two categories of identical molecules.

The foregoing derivation of the paradox does not differ essentially from Gibbs' original discussion (ref. [4] p. 166) as well as those of standard textbooks of Rocard (ref. [6] p. 25) and Finkelstein (ref. [7] p. 160). All these discussions point to a hidden fallacy introduced in the formulation namely that identical molecules may be distinguished by a physical process.

6. Extension of the Gibbs–Duhem theorem

In the foregoing development we have assumed that m_k represent masses of the pure substances added to a primary cell without specifying the initial contents of cell. We shall now assume that the cell is constituted exclusively by a fluid mixture of the pure substances and that m_k denotes the total mass of each substance in the cell. Following a procedure already originated by Gibbs (ref. [4] p. 87) we start with a cell of vanishing volume with given values of the pressure p temperature T and concentrations:

$$\mathcal{C}_k = m_k \Big/ \sum_k m_k \,. \tag{6.1}$$

We maintain constant $p, \theta, \mathcal{C}_k$ while we inject masses into the cell by thermobaric transfer. Under these conditions the partial pressures p_k and the specific relative entropies $\bar{s}_k$ of the pure substances remain constant. Hence the convective potentials ϕ_k also remain constant. With these constant values we integrate expression (4.12) putting $\mathcal{V} = \mathcal{S} = v = m_k = 0$ in the initial state of zero mass. This yields

$$\mathcal{V} = -pv + \sum_k \phi_k m_k + \theta\mathcal{S} \,. \tag{6.2}$$

Since we start with arbitrary values of p, ϕ_k and θ this expression for $\mathcal{V}$ is quite general and is valid for arbitrary values of v, m_k and $\mathcal{S}$.

An important consequence of this result is obtained by differentiating eq. (6.2) i.e.

$$\mathrm{d}\mathcal{V} = -p\,\mathrm{d}v - v\,\mathrm{d}p + \sum_k \phi_k \mathrm{d}m_k + \sum_k m_k\, \mathrm{d}\phi_k + \theta\,\mathrm{d}\mathcal{S} + \mathcal{S}\,\mathrm{d}\theta \,. \tag{6.3}$$

If the nonpotential forces perform no work ($W'_{\mathrm{P}} = 0$) we derive the important relation

$$\mathcal{P} = -T_0 S' . \tag{7.10}$$

In the equilibrium state variations which satisfy the required constraints produce no entropy. Hence the equilibrium condition is

$$\delta\mathcal{P} = \delta S' = 0 . \tag{7.11}$$

In the vicinity of equilibrium the increase of $\mathcal{P}$ is

$$\Delta\mathcal{P} = -T_0 \Delta S' . \tag{7.12}$$

Since the entropy produced $\Delta S'$ is positive, $\Delta\mathcal{P}$ must be negative and the system is in *unstable equilibrium*. On the other hand, if $\Delta\mathcal{P}$ is positive in the vicinity of equilibrium the deviation cannot occur and the equilibrium is stable.

We have considered a finite number of primary cells, however we may consider a continuous primary system. The primary cells are then infinitesimal and the summation in eq. (7.2) is replaced by a volume integral. The collective potential is

$$V = \int_\Omega \mathcal{V} \mathrm{d}\Omega , \tag{7.13}$$

where $\mathrm{d}\Omega = \mathrm{d}x_1 \mathrm{d}x_2 \mathrm{d}x_3$ is the volume element with cartesian coordinates x_i and $\mathcal{V}$ is the local cell potential per unit volume. The value of G is

$$G = \int_\Omega \rho \mathcal{G} \, \mathrm{d}\Omega , \tag{7.14}$$

where ρ is the mass per unit volume and $\mathcal{G}(x_i)$, a function of the coordinates, is a body force potential per unit mass. We assume the outlets of the supply cells to be located on the equipotential surface $\mathcal{G} = 0$. The generalized collective potential (7.7) is

$$\mathcal{P} = \int_\Omega (\mathcal{V} + \rho\mathcal{G}) \, \mathrm{d}\Omega . \tag{7.15}$$

We assume that this continuous medium is contained in a rigid adiabatic vessel. Introducing expression (4.12) for $\delta\mathcal{V}$ the equilibrium condition is

$$\delta\mathcal{P} = \int_\Omega \Big[-p\delta v + \sum_k \phi_k \delta m_k + \theta\delta\mathcal{S} + \rho\delta\mathcal{G} + \mathcal{G}\delta\rho \Big] \mathrm{d}\Omega = 0 , \tag{7.16}$$

where δm_k are the variations of the masses of various substances per unit volume, hence also

$$\delta\rho = \sum_k \delta m_k . \tag{7.17}$$

Eq. (7.16) must be valid for arbitrary variations. Let us first vary the volume putting $\delta m_k = \delta\mathcal{S} = 0$. The volume variation is

$$\delta v = \sum_i (\partial/\partial x_i) \, \delta u_i , \tag{7.18}$$

where δu_i are arbitrary material displacements. Also

$$\delta\mathcal{G} = \sum_i (\partial\mathcal{G}/\partial x_i) \delta u_i . \tag{7.19}$$

Substitution of eqs. (7.18) and (7.19) in eq. (7.16) yields after integration by parts

$$\rho^{-1} \, \partial p/\partial x_i + \partial\mathcal{G}/\partial x_i = 0 , \tag{7.20}$$

which is an obvious static equilibrium condition. We now vary m_k and $\mathcal{S}$ and put $\delta v = 0$ with the constraints

$$\int_\Omega \delta m_k \, \mathrm{d}\Omega = \int_\Omega \delta\mathcal{S} \, \mathrm{d}\Omega = 0 , \tag{7.21}$$

which express mass conservation and no variation of the total entropy. These constraints are verified identically if we put

$$\delta m_k = \sum_i (\partial/\partial x_i) \delta E_i^k , \quad \delta\mathcal{S} = \sum_i (\partial/\partial x_i) \delta F'_i , \tag{7.22}$$

where δE_i^k and $\delta F'_i$ are arbitrary vectors with zero normal components at the boundary of Ω. Substitution of expressions (7.22) into (7.16) yields after integration by parts

$$(\partial/\partial x_i)(\phi_k + \mathcal{G}) = 0 , \quad \partial\theta/\partial x_i = 0 . \tag{7.23}$$

Hence at equilibrium $\phi_k + \mathcal{G}$ and the temperature T are constant throughout the domain Ω. From eq. (4.16) with $\partial T/\partial x_i = 0$ we derive

$$\partial\phi_k/\partial x_i = (1/\rho_k) \, \partial p_k/\partial x_i . \tag{7.24}$$

Hence from (7.23)

$$(1/\rho_k) \, \partial p_k/\partial x_i + \partial\mathcal{G}/\partial x_i = 0 . \tag{7.25}$$

Thus we conclude that *the partial pressure gradients of each substance in the mixture is the same as if the pure substance were alone in the potential field* $\mathcal{G}$

with a suitable choice of average density. Partial pressures are therefore constant on equipotential surfaces. This result is completely general and does require the substances to be perfect gasses. If there is no body force field ($\mathcal{G} = 0$) the partial and total pressures are uniform throughout.

8. Comparison with Gibbs' work and standard potentials

At this point some comparison is in order with the classical concepts and methods introduced by Gibbs. He starts with an expression which in his notation (ref. [4] p. 63) is written

$$\mathrm{d}\epsilon = T\mathrm{d}\eta - p\,\mathrm{d}v + \sum_k \mu_k\,\mathrm{d}m_k\,. \tag{8.1}$$

He calls ϵ the energy of an open homogeneous cell at the temperature T, pressures p, volume v and entropy η while $\mathrm{d}m_k$ are the masses of the various pure substances added to it. Gibbs' chemical potentials μ_k *are then by definition the differential coefficients of* $\mathrm{d}m_k$ in eq. (8.1) which is known as the Gibbs equation. The value of μ_k is thus obtained by evaluating $\mathrm{d}\epsilon$ for $\mathrm{d}\eta = \mathrm{d}v = 0$. According to Gibbs' statement (ref. [4] p. 95) this is accomplished by bringing into the primary cell a unit mass of the pure substance from a initial state by a reversible process and the mechanical work in this process is equal to μ_k. Upon completion of the process all masses involved except the primary cell are returned to their original states. The original entropy of the added mass is chosen to be zero and the process being reversible no change in entropy η occurs by the addition of the substance to the primary cell.

The difference with our procedure is immediately evident. Elimination of $\mathcal{V}$ between eqs. (3.5) and (4.12) for an open primary cell yields

$$\mathrm{d}\mathcal{U} = T\mathrm{d}\mathcal{S} - p\,\mathrm{d}v + \sum_k \phi_k\,\mathrm{d}m_k\,. \tag{8.2}$$

While similar to Gibbs' eq. (8.1) its significance is fundamentally different. In the first place $\mathcal{U}$ and $\mathcal{S}$ are the collective energy and entropy of the combined set of primary and supply cells. They are given a precise definition within the framework of classical thermodynamics for closed systems since no matter is added to the system. In addition the convective potentials ϕ_k are defined independently from eq. (8.2) by eq. (4.13) based on the concept of a thermobaric potential. Hence eq. (8.2) in contrast with eq. (8.1) does not define ϕ_k but constitutes a theorem. Also in contrast with Gibbs' procedure the supply cells do not return to their initial states after the mass transfer is completed and the work of extraction from the supply cells is taken into account in the collective energy $\mathcal{U}$. Another fundamental difference is brought out by eq. (4.9) for the entropy differential $\mathrm{d}\mathcal{S}$ which shows that it is not independent of $\mathrm{d}m_k$. It contains a term $\Sigma_k\,\bar{s}_k\,\mathrm{d}m_k$ which represents the increase of entropy of the primary cell due to convection, so that a reversible transfer of masses does not imply $\mathrm{d}\mathcal{S} = 0$. This point was completely overlooked by Gibbs.

There is also the question of indeterminacy of μ_k which contains an arbitrary constant for each substance. This point was recognized by Gibbs' himself (ref. [4] p. 96). The difficulty has remained until today as pointed out in standard textbooks. For example, Hatsopoulous and Keenan (ref. [2] p. 278) state that a characteristic of the chemical potential is its indeterminateness for a change in temperature, so that changes in chemical potential are determined experimentally only at constant temperature. Prigogine and Defay (ref. [8] p. 66) bypass these difficulties by "presuming" that the energy and entropy of an open cell may be expressed in terms of the masses added using statistical concepts when needed. In our definition of the convective potentials ϕ_k in the context of a given hypersystem no indeterminacy occurs.

Note that we may derive a function analogous to Gibbs free energy for a primary cell by putting

$$\mathcal{F} = \mathcal{V} + pv - \mathcal{S}\theta\,. \tag{8.3}$$

From the value (3.5) of $\mathcal{V}$ we derive

$$\mathcal{F} = \mathcal{U} - T\mathcal{S} + pv\,, \tag{8.4}$$

where v is the volume of the cell. This expression differs from the standard potential by the fact that $\mathcal{U}$ and $\mathcal{S}$ are the collective energy and entropy and do not involve any indeterminacy due to arbitrary constants.

9. Application to chemical reactions

The concept of thermobaric transfer may be applied to analyse the case where a chemical reaction occurs in the primary cell. New formulas for the affinity and the heat of reaction are obtained. Although already presented earlier [1] these formulas were derived by a slightly different reasoning. The method presented here evaluates the entropy produced by the chemical reaction entirely within the framework of classical thermodynamics and without any recourse to statistical mechanics.

Consider a reaction occurring in a primary cell. The masses of the various reactants "produced" by the reaction are

$$\mathrm{d}m_k = \nu_k \, \mathrm{d}\xi \,, \tag{9.1}$$

where ξ is the reaction coordinate. Conservation of mass requires the condition

$$\sum_k \nu_k = 0 \,. \tag{9.2}$$

Hence some terms are negative. For convenience if $\mathrm{d}\xi > 0$ we shall call $\mathrm{d}m_k$ the masses "produced" whether they are positive or negative. In order to extend the concept of collective potential to this case we consider a hypersystem constituted by a primary cell $\mathrm{C_P}$, a thermal well TW and a reference chemical cell $\mathrm{C_{ch}}$ (fig. 4). The cell $\mathrm{C_{ch}}$ is a large rigid reservoir at the pressure p' and temperature T', where the reacting substances are in chemical equilibrium. It is large enough so that a chemical reaction does not affect significantly the total pressure p, the temperature T or the partial pressures p'_k of the pure substances in the cell.

We shall also need a new definition of the heat of reaction already introduced earlier [1]. Consider a reaction $\mathrm{d}\xi$ occuring in a rigid primary cell and let us remove the products of reaction so that the composition of the cell does not change. At the same time we maintain a constant temperature by providing heat to the cell. As a consequence the total pressure also remains constant. Under these conditions the heat provided to the cell is denoted by

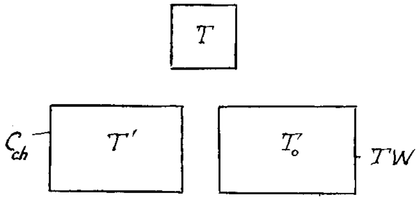

Fig. 4. Hypersystem constituted by a primary cell Cp a reference chemical cell $\mathrm{C_{ch}}$ at the temperature T' and a thermal well TW.

$$\bar{h}_{pT} \, \mathrm{d}\xi \,, \tag{9.3}$$

where $\bar{h}_{pT}$ will be called the *intrinsic heat* of reaction at constant pressure and temperature. It excludes the heat of mixing. The standard heat of reactions is

$$h_{pT} = \bar{h}_{pT} + \sum_k \nu_k \, h^k_{pT} \,, \tag{9.4}$$

where h^k_{pT} is the heat of mixing as defined by eq. (5.2).

The intrinsic heat of reaction $\bar{h}_{pT}$ is more representative of the true chemical energy than h_{pT} since it does not involve the heat of mixing.

We now assume a forward reaction $\mathrm{d}\xi$ in the chemical cell $\mathrm{C_{ch}}$ and a simultaneous backward reaction $-\mathrm{d}\xi$ in the primary cell $\mathrm{C_P}$. The products of reaction of masses $\nu_k \, \mathrm{d}\xi$ are extracted from $\mathrm{C_{ch}}$ and injected into $\mathrm{C_P}$ by thermobaric transfer. At the same time using heat pumps amounts of heat $\bar{h}'_{p'T'} \, \mathrm{d}\xi$ and $-\bar{h}_{pT} \, \mathrm{d}\xi$ are fed into $\mathrm{C_{ch}}$ and $\mathrm{C_P}$ respectively. We denote by $\bar{h}'_{p'T'}$ the heat of reaction in $\mathrm{C_{ch}}$ and by $\bar{h}_{pT}$ the heat of reaction in $\mathrm{C_P}$. Under these conditions the composition temperature and pressure of the cells $\mathrm{C_P}$ and $\mathrm{C_{ch}}$ remain constant. Hence the collective energy U does not vary. This is expressed by

$$\mathrm{d}U = (\bar{h}'_{p'T'} - \bar{h}_{pT}) \, \mathrm{d}\xi$$

$$+ \, \mathrm{d}\xi \sum_k \nu_k \int_{p'_k T'}^{p_k T} (\mathrm{d}p_k/\rho_k + T \, \mathrm{d}\bar{s}_k) = 0 \,. \tag{9.5}$$

The first term in the integration represents the work done on the masses transferred, while the second term is the heat injected into these masses. In the integrand p_k and T are the variable pressure and temperature of the masses being transferred while in the upper limit they represent the partial pressures and the temperature in $\mathrm{C_P}$. In the lower limit p'_k and T' are the partial pressures and temperature in the reference chemical cell $\mathrm{C_{ch}}$. From eq. (9.5) we derive

$$\bar{h}_{pT} - \bar{h}'_{p'T'} = \sum_k \nu_k \int_{p'_k T'}^{p_k T} (\mathrm{d}p_k/\rho_k + T \, \mathrm{d}\bar{s}_k) \,. \tag{9.6}$$

This new and very general expression for the intrinsic heat of reaction was already obtained earlier [1]. Note that its validity does not require the reference chemical cell to be in equilibrium.

If we perform the same mass and heat transport process after freezing the reaction in C_P, the injection of heat $-\bar{h}_{pT}\,d\xi$ and masses $\nu_k\,d\xi$ induces a change of state in C_P which is the same as if the chemical reaction has taken place in the rigid cell without any addition of mass or heat from outside the cell. Also the state of the chemical cell C_{ch} remains unchanged. Furthermore since the chemical cell C_{ch} is assumed to be in equilibrium, this modified transport process becomes a reversible transformation thermodynamically equivalent to the chemical reaction. The increase of the collective potential $d\mathcal{V}$ in this process according to our definition of section 3 is the associated reversible work on the hypersystem by applied forces and heat pumps. According to eq. (3.17) with $dv = 0$, this reversible work is

$$d\mathcal{V} = d\xi \sum_k \nu_k \int_{p'_k T'}^{p_k T} (dp_k/\rho_k + \theta\, d\bar{s}_k)$$

$$+ (\theta' \bar{h}'_{p'T'}/T - \theta \bar{h}_{\mathrm{pT}}/T)\, d\xi\,, \tag{9.7}$$

where $\theta = T - T_0$ and $\theta' = T' - T_0$. By rearranging the terms and taking into account eq. (9.6) we may write

$$d\mathcal{V} = -(T_0/T)\, A\, d\xi\,, \tag{9.8}$$

where

$$A/T = \sum_k \nu_k \int_{p'_k T'}^{p_k T} d\bar{s}_k + \bar{h}'_{p'T'}/T' - \bar{h}_{pT}/T\,. \tag{9.9}$$

The quantity $(A/T)\,d\xi$ is obviously the increase of collective entropy in the modified reversible transport process. Hence it is also the entropy *produced* when an irreversible chemical reaction $d\xi$ occurs in a rigid isolated primary cell. We may call A the affinity of the reaction since this is compatible with the definition introduced by de Donder [9]. However, in the present case a new formula (9.9) is obtained for A as already derived previously [1]. (Note the misprint in eq. (7.23) of ref. [1]). Expression (9.9) for the affinity and entropy produced involves only mechanical and calorimetric concepts and does not make any use of statistical concepts as in the standard procedures.

Elimination of $\bar{h}_{pT}$ between relations (9.6) and (9.9) yields

$$A = \sum_k \nu_k T \int_{p'_k T'}^{p_k T} d\bar{s}_k - \sum_k \nu_k \int_{p'_k T'}^{p_k T} (dp_k/\rho_k + T d\bar{s}_k)$$

$$+ (T/T' - 1)\, \bar{h}_{p'T'}\,, \tag{9.10}$$

which may be compared with the expression given by Prigogine and Defay (ref. [8] p. 50 eq. (4.17)) which is less general and valid only when the temperature is varied.

Denoting the entropy produced by

$$d\mathcal{S}_{ch} = (A/T)\, d\xi\,, \tag{9.11}$$

we may write eq. (9.8) in the form

$$d\mathcal{V} = -A\, d\xi + \theta\, d\mathcal{S}_{ch}\,. \tag{9.12}$$

For a frozen chemical reaction the increase of the collective potential (4.12) is given by

$$d\mathcal{V} = -p\, dv + \sum_k \phi_k\, dM^k + \theta\, d\mathcal{S}'\,, \tag{9.13}$$

where dM^k now represent masses which do not participate in the reaction and are injected into the primary cell from the outside by thermobaric transfer. The total increase of masses due to those acquired by convection and by the chemical reaction is

$$dm_k = \nu_k\, d\xi + dM^k\,. \tag{9.14}$$

The total increase in the collective cell potential is obtained by adding expressions (9.12) and (9.13). We obtain

$$d\mathcal{V} = -A\, d\xi - p\, dv + \sum_k \phi_k\, dM^k + \theta\, d\mathcal{S}\,, \tag{9.15}$$

where the collective entropy increase of the cell is

$$d\mathcal{S} = d\mathcal{S}_{ch} + d\mathcal{S}' = AT^{-1}\, d\xi + \sum_k \bar{s}_k\, dM^k + ds_T\,. \tag{9.16}$$

10. Classical results for reacting perfect gasses

For mixtures of perfect gasses we shall obtain a new very simple derivation of classical results. The equation of state of the pure substance is

$$p_k = \rho_k R \mathcal{M}_k^{-1} T \, , \tag{10.1}$$

where $\mathcal{M}_k$ is the molecular weight and R the universal molar gas constant. From (5.14) the entropy differential is

$$\mathrm{d}\bar{s}_k = \mathcal{M}_k^{-1}[c_{kp}(T)T^{-1}\mathrm{d}T - (R/p_k)\,\mathrm{d}p_k] \, , \tag{10.2}$$

where c_{kp} is the molar specific heat at constant pressure. Combining (10.1) and (10.2) we derive

$$\mathrm{d}p_k/\rho_k + T\,\mathrm{d}\bar{s}_k = \mathcal{M}_k^{-1} c_{pk}(T)\,\mathrm{d}T \, . \tag{10.3}$$

For perfect gasses the heat of mixture vanishes, hence

$$h_{pT} = \bar{h}_{pT} \, . \tag{10.4}$$

The heat of reaction is the same and equal to the standard definition whether we remove or not the products of reaction. Substitution of expressions (10.3) and (10.4) into (9.6) yields

$$h_{pT} - h'_{p'T'} = \sum_k \nu'_k \int_{T'}^{T} c_{kp}(T)\,\mathrm{d}T \, , \tag{10.5}$$

where

$$\nu'_k = \nu_k \mathcal{M}_k^{-1} \tag{10.6}$$

are the stoichiometric coefficients. Eq. (10.5) coincides with the classical *Kirchhoff relation* when applied to perfect gasses.

By substituting expression (10.2) and (10.3) into the value (9.10) of the affinity we obtain

$$A = RT\log[K(T)/p_1^{\nu'_1} p_2^{\nu'_2} \dots p_k^{\nu'_k}] \, , \tag{10.7}$$

where we have put

$$RT\log K(T) =$$

$$T\sum_k \nu'_k \int_{T'}^{T} c_{kp}(T)T^{-1}\mathrm{d}T - \sum_k \nu'_k \int_{T'}^{T} c_{kp}(T)\,\mathrm{d}T$$

$$+ RT\sum_k \nu'_k \log p'_k + (T/T' - 1)\,h'_{p'T'} \, . \tag{10.8}$$

For a given reference chemical cell, $K(T)$ thus defined is a function only of the temperature T.

For chemical equilibrium the entropy production must vanish, hence $A = 0$. In this case eq. (10.7) yields

$$p_1^{\nu'_1} p_2^{\nu'_2} \dots p_k^{\nu'_k} = K(T) \, , \tag{10.9}$$

where $K(T)$ is the equilibrium constant.

For a mixture of prefect gasses the partial pressures p_k are

$$p_k = p\gamma_k \, , \tag{10.10}$$

where p is the total pressure of the mixture and γ_k are the molar fractions. Hence eq. (10.9) becomes

$$p^{-\nu'} K(T) = \gamma_1^{\nu'_1} \gamma_2^{\nu'_2} \dots \gamma_k^{\nu_k} \, , \tag{10.11}$$

where $\nu' = \Sigma_k \nu'_k$. Eq. (10.11) expresses the law of *Guldberg and Waage* for chemical equilibrium.

Another classical result is obtained by taking the derivative of eq. (10.8) with respect to the temperature after dividing the equation by T. Taking into account Kirchhoffs relation (10.5) we obtain

$$(\mathrm{d}/\mathrm{d}T)\log K(T) = h_{pT}/RT^2 \, . \tag{10.12}$$

This is the classical *van't Hoff* relation.

11. Generalized van't Hoff–le Chatelier principle

The problem of displacement of chemical equilibrium of an open cell under variations of pressure, temperature and masses injected is immediately resolved using the foregoing results. We consider the state of the open cell to be defined by its pressure p, its temperature T, the reaction variable ξ and the masses M^k of substances injected. Partial derivatives with respect to any of these variables imply that the other three remain constant. The entropy produced by the reaction is

$$s^* = T^{-1} \int_{\xi_0}^{\xi} A\,\mathrm{d}\xi \, , \tag{11.1}$$

where ξ_0 is the value of ξ at equilibrium ($A = 0$). To the second order eq. (11.1) may be written

$$s^* = \tfrac{1}{2} T^{-1} (\xi - \xi_0)^2 \partial A/\partial \xi \, . \tag{11.2}$$

Stability requires that the entropy produced decreases for any departure from equilibrium, hence

$$\partial A/\partial \xi < 0 \, . \tag{11.3}$$

Since A is a function of p, T, ξ and M^k, maintaining equilibrium requires.

$$\mathrm{d}A = \frac{\partial A}{\partial p}\mathrm{d}p + \frac{\partial A}{\partial T}\mathrm{d}T + \frac{\partial A}{\partial \xi}\mathrm{d}\xi + \sum_k \frac{\partial A}{\partial M^k}\mathrm{d}M^k = 0 \, . \tag{11.4}$$

By adding $d(pv - \theta\mathcal{S})$ to eq. (9.15) we obtain the exact differential

$$d(\mathcal{V} + pv - \theta\mathcal{S}) = v\,dp - \mathcal{S}\,dT - A\,d\xi + \sum_k \phi_k dM_k \,. \tag{11.5}$$

This implies

$$\frac{\partial A}{\partial p} = -\frac{\partial v}{\partial \xi}\,, \quad \frac{\partial A}{\partial T} = \frac{\partial \mathcal{S}}{\partial \xi}\,, \quad \frac{\partial A}{\partial M^k} = -\frac{\partial \phi_k}{\partial \xi}\,. \tag{11.6}$$

Also be definition

$$\partial\mathcal{S}/\partial\xi = h_{pT}/T\,, \tag{11.7}$$

where h_{pT} is the standard heat of reaction at constant pressure and temperature. With the values (11.6) and (11.7) eq. (11.4) becomes

$$\frac{\partial A}{\partial \xi} d\xi = \frac{\partial v}{\partial \xi} dp - \frac{h_{pT}}{T} dT + \sum_k \frac{\partial \phi_k}{\partial \xi} dM^k \,. \tag{11.8}$$

Consider the case where we increase the pressure p, the temperature T, and the masses injected M^k either separately or simultaneously, i.e. we put

$$dp \geqslant 0\,, \quad dT \geqslant 0\,, \quad dM^k \geqslant 0\,. \tag{11.9}$$

Since $\partial A/\partial\xi < 0$ the reaction will regress ($d\xi < 0$) if

$$\partial v/\partial\xi > 0\,, \quad -h_{pT} > 0\,, \quad \partial\phi_k/\partial\xi > 0\,, \tag{11.10}$$

hence if the forward reaction ($d\xi$) increases the volume, is exothermic and increases the convective potential ϕ_k of the particular substance injected.

This constitutes a generalized form of the van't Hoff–le Chatelier principle for open systems in terms of the new convective potential. The simplicity and generality of the present derivation must be compared with the more restricted form of the principle as treated in standard textbooks (e.g. see [8] p. 271).

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