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EXTRAIT

New Chemical Thermodynamics of open Systems. Thermobaric potential, a new Concept

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Abstract. — A fundamentally new approach to the chemical thermodynamics of open systems is presented. It is based on a new concept referred to here as the *thermobaric potential*. The usual difficulties associated with open systems are eliminated by considering a closed system where supply cells provide matter transferred internally. The procedure requires only mechanical and calorimetric concepts. Use of statistical mechanics or Nernst's theorem is completely avoided without leading to Gibbs's paradox. A new chemical potential is obtained as well as new and completely general expressions for the affinity and heat of reaction in terms of mechanical and calorimetric measurements. The heat of reaction is defined in a new way which excludes the heat of mixing and is more representative of the chemical energy than the current definition. Application to perfect gasses yields classical results with great clarity and simplicity.

1. INTRODUCTION

In the classical thermodynamics of open systems which exchange matter with the environment the definition of internal energy and entropy has always been the source of difficulties such as Gibbs' paradox. This is due to the fact that from the classical viewpoint these quantities are defined in terms of *increments* of heat or work absorbed by a given amount of matter as a closed system. The difficulties may be partly surmounted by introducing statistical concepts and the properties of matter near the absolute zero through Nernst's theorem. We will show here that this procedure is not necessary and that the difficulties, including Gibbs's paradox, may be avoided by using exclusively classical concepts.

The principle of the method is to use a closed physical system constituted by a primary cell and a serie of supply cells each containing one of the pure substances present in the mixture in the primary cell. We also adjoin a large isothermal reservoir at constant temperature called a *thermal well*. The primary and supply cells constitute a collective system and possess a *collective potential* already defined [1-2] and used many times earlier by the author. Matter is transferred from the supply cells to the primary cell by a *reversible process* which we have called a *thermobaric transfer*. It leads to a new concept, the *thermobaric potential*. The key to the procedure lies in the fact that the thermobaric transfer is accomplished by the use of mechanical pumps and heat pumps on the material belonging to the collective system.

It is shown how the heat pumps do not require the use of material cycles but may use *pure black body radiation*.

Hence while the primary cell is open, the collective system is not, and may be treated exclusively by classical methods.

The concept of collective potential which is fundamental in the procedure also provides the basic concept in the principle of virtual dissipation introduced by the author [2] as a generalization of d'Alembert's principle to nonlinear irreversible thermodynamics.

The concept of thermobaric transfer leads to a new chemical potential. Application to chemical reactions provides new expressions for the affinity and the heat of reaction. The latter is also defined in a new way which is more representative of the true chemical energy since it does not contain the heat of mixing. The results do not assume any perfect gas property. When applied to perfect gasses they yield immediately and very simply all the classical relations.

2. The concept of collective potential

The principle of virtual dissipation developed in detail in an earlier publication [2] uses what we have referred to as the collective potential

$$V = U - T_o S \tag{2.1}$$

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where U is the internal energy, and S the entropy of the collective system while T_a is the constant temperature of a large adjoined isothermal reservoir which we have called a thermal well. The term hypersystem denotes the combined system constituted by the collective system and the thermal well. When originally introduced in 1954-55 [1] the term generalized free energy was used for V. The term collective potential is to be preferred because it emphasizes the non homogeneous character of the system which is not isothermal and may be composed of a large or infinite number of cells of different properties. Expression (2.1) in this context as a true thermodynamic potential with new highly useful properties as derived by the author [2] is to be distinguished from the concept of "availability" which has been known in the classical litterature as a mean of expressing the balance of available energy including a term dependent on atmospheric pressure. A crucial advantage of the collective potential over the classical potentials of Gibbs and Helmholtz is the property of addivity which is expressed by the relation

$$\mathbf{V} = \sum_{\alpha}^{\alpha} \mathscr{V}_{\alpha} \tag{2.2}$$

This relation applies to the case where the collective system is composed of any number of cells each cell having an internal energy U_{α} and entropy \mathscr{S}_{α} while

$$\mathscr{V}_{\alpha} = \mathrm{U}_{\alpha} - \mathrm{T}_{o}\mathscr{S}_{\alpha} \tag{2.3}$$

is called the cell potential. The cells may be infinitesimal and infinite in number, thus representing a continuum. The summation $\sum_{i=1}^{a}$ in this case is replaced by a volume integral.

In the analysis which follows we shall introduce two different meanings for the term cell potential. A *closed cell potential* discussed in section 3 considers a closed cell. A generalized concept of *open cell potential* introduced in section 4 describes the properties of an open cell.

Another important property of the collective potential is obtained as follows. Let dW be the work done by external forces on the collective system. In the absence of inertia forces, conservation of energy implies,

$$d\mathbf{U} = d\mathbf{W} - d\mathbf{H}_o \tag{2.4}$$

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where dH_{α} is the heat energy lost by the collective system. Assuming the hypersystem to be an isolated system the heat energy dH_o must be absorbed by the thermal well whose entropy increase is

$$dS_o = \frac{dH_o}{T_o}$$
(2.5)

We eliminate dU and dH_o between equations (2.1) (2.4) and (2.5). This yields

$$d\mathbf{V} - d\mathbf{W} = -\mathbf{T}_o d\mathbf{S}' \tag{2.6}$$

where $S' = S + S_o$ is the total entropy of the hypersystem. This relation is valid for any transformation reversible or not.

It should be noted that equation (2.6) relating the collective potential and the work done to the total entropy produced in the hypersystem was already used by the author in 1955 [1] and subsequent work, in a more restricted context.

3. CLOSED CELL POTENTIAL. MATERIAL AND RADIATION HEAT PUMPS

Consider a single closed cell, i.e. one such that matter is not exchanged with the environment. We shall call it the primary cell and its potential is denoted by \mathscr{V} . We adjoin to this cell an auxiliary cell of potential \mathscr{V}' by which, using a reversible heat pump process, we transfer heat from the thermal well to the primary cell. The combined primary and auxiliary cell constitute a collective system of collective potential,

$$\mathbf{V} = \mathscr{V}' + \mathscr{V} \tag{3.1}$$

We may apply equation (2.6) and write

$$d\mathbf{V} - d\mathbf{W} = d\mathscr{V}' + d\mathscr{V} - d\mathbf{W} = -\mathbf{T}_o d\mathbf{S}'$$
(3.2)

Since the process is reversible the total entropy change of the hypersystem vanishes, hence

$$d\mathbf{S}' = \mathbf{0} \tag{3.3}$$

We assume that the process is quasi-static hence there are no inertia forces. The total work on the collective system may be written

$$dW = dW_p + dW_H$$
(3.4)
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where dW_p is the work of the forces applied to the primary cell while is the work accomplished by the heat pumps. Substitution of the values (3.3) and (3.4) into (3.2) yields

$$d\mathscr{V}' + d\mathscr{V} = dW_p + dW_H \tag{3.5}$$

The heat pumps may be of two types. In one case we use as auxiliary cell a small amount of matter actually infinitesimal which undergoes a closed reversible Carnot cycle extracting heat from the thermal well an injecting a certain amount of heat *dh* reversibly at the temperature T into the primary cell. The pump may of course be reversed, acting like and engine extracting a heat energy *dh* from the primary cell. After each closed cycle $d\mathcal{V}' = 0$ and we may write (3.2) as

$$d\mathscr{V} = dW_p + dW_H \tag{3.6}$$

Hence the change of cell potential is the sum of the work done directly on the cell and the work of the heat pump.

BLACK BODY RADIATION HEAT PUMP

It is interesting to note that the pump does not require the use of matter as an auxiliary cell. The reversible heat transfer to the primary cell may be accomplished using only black body radiation. In this case the auxiliary cell may be a small cylinder with a pison. Strictly speaking in the limit this auxiliary cell is infinitesimal. The flat base opposite the piston contains a thermal window which becomes pervious to heat when opened. When it is closed the cell provides a completely reflecting cavity. We start with the thermal window against the thermal well and the piston against the window, so that the cavity volume is zero. We then open the thermal window and slowly move the piston creating a cavity being filled with black body radiation at a pressure corresponding to the thermal well temperature T_e. The piston in this process performs negative work against the radiation pressure. The thermal window is then closed and the piston is moved to compress the black body radiation adiabatically until a radiation pressure is reached corresponding to the temperature T of the primary cell. The thermal window is then applied against the primary cell and opened. Moving the piston slowly until the volume of the cavity is zero, the

black body radiation is injected into the primary cell and again the piston does work against the radiation pressure. Through this entire reversible process the auxiliary cell starts and finishes with zero cavity volume so that the variation $d\mathscr{N}'$ of its cell potential vanishes. Hence we may apply equation (3.6) where $dW_{\rm H}$ now represents the total work accomplished on the black body radiation in the extraction from the thermal well, its adiabatic compression and its injection into the primary cell.

HEAT PUMP ENERGY

An expression of considerable importance may be obtained for $dW_{\rm H}$, by using energy conservation equation for the primary cell. For a reversible process it is written

$$d\mathbf{U} = \mathbf{T}ds + d\mathbf{W}_{\mathbf{p}} \tag{3.7}$$

where U is the internal energy of the primary cell and ds the entropy supplied to it reversibly by conduction. For a closed cell and a reverssible process, $d\mathcal{S} = ds$ and by definition (2.3) we may write

$$d\mathscr{V} = d\mathbf{U} - \mathbf{T}_{o}ds \tag{3.8}$$

Substitution of the value (3.7) for dU yields

$$d\mathscr{V} = dW_p + \theta ds \tag{3.9}$$

with

$$\theta = T - T_o \tag{3.10}$$

Comparing with (3.6) we obtain for the work of the heat pump

$$dW_{\rm H} = \theta ds \tag{3.11}$$

For a reversible process the entropy variation is

$$ds = \frac{dh}{T} \tag{3.12}$$

where dh is the heat injected into the primary cell. Hence

$$dW_{\rm H} = \frac{\theta}{\rm T} dh \tag{3.13}$$

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This is in accordance with the classical result for the efficiency of a reversible heat engine where θ/T is the Carnot efficiency. This result is valid for either the Carnot cycle heat pump or the radiation heat pump.

4. OPEN CELL POTENTIAL. THERMOBARIC POTENTIAL, A NEW CONCEPT

The foregoing analysis does not specify how the cell potential is to be defined for open cells, i.e. for the case where matter may be added or extracted from the cell. The case for open systems has always given rise to fundamental difficulties in classical thermodynamics. We intend to develop a novel approach to open system which avoids these difficulties.

We shall consider a rigid cell of constant volume which will be referred to as the primary cell. This cell contains a mixture of various chemical species each being denoted by the subscript k. For simplicity we shall assume that the mixture and the pure substance are fluids in the range of temperatures considered. Actually this assumption is not essential and is only a matter of convenience as will be shown below. The state of the cell is defined by the masses m_k of the various components in the cell, and by any two of the following variables; volume temperature and mixture pressure. For the time being we also assume that no chemical reaction occurs in the mixture. The case of a reacting mixture will be considered below in sections 6 and 7.

In order to define a suitable potential for an open cell we consider a collective system obtained by adding cells constituted by large *rigid* thermally insulated reservoirs each containing a pure substance at the same pressure p_o and the same temperature T_o equal to that of the thermal well. We shall call these cells the *supply cells*.

As part of the collective system we also add a small auxiliary cell with a piston whose motion may generate a cavity of zero volume initially. Strictly speaking we must consider the auxiliary cell to be infinitesimal in the limit. This is entirely similar to the auxiliary cell considered in the previous section in connection with the radiation heat pump.

The auxiliary cell will be used as a pump to extract masses from the supply cells and inject them into the primary cell by a reversible process. Consider the injection into the primary cell of a mass dm_k of substance k. We proceed in three steps.

First the auxiliary cell is made to communicate with the corresponding supply cell, the piston is then moved until the auxiliary cell contains a mass dm_k at the pressure p_a . The work done by the piston is

$$dW_{I} = -\frac{p_{o}}{\rho_{ok}} dm_{k}$$
(4.1)

where ρ_{ok} is the density of the substances k at the pressure p_o and temperature T_o . We apply equation (3.9) to the system of the supply cell and the auxiliary cell considered as a closed system. Since the supply cell is rigid and thermally insulated the increase of collective potential is

$$d\mathbf{V}_{\mathbf{I}} = d\mathbf{W}_{\mathbf{I}} = -\frac{p_o}{\rho_{ok}} dm_k \tag{4.2}$$

We now close the auxiliary cell. By moving the piston and heating the fluid in a reversible process by heat pumps we bring it to the pressure p_k and the temperature T. Again we apply equation (3.9). The increase of potential of the auxiliary cell in this process is

$$d\mathbf{V}_{\mathrm{II}} = dm_k \int_{p_o T_o}^{p_k T} \left[p_k d\left(\frac{1}{\rho_k}\right) + \theta d\bar{s}_k \right]$$
(4.3)

The first term in the integral represents the work done by the piston on a unit mass of fluid, and $d\bar{s}_k$ represents the entropy increase of a unit mass of substance k, during the process of heat pumping. In the integral

$$\rho_k = \rho_k(\mathbf{T}, p_k) \tag{4.4}$$

is the density of the pure substance function of its pressure p_k and temperature T. For simplicity, we use the same notation p_k , T, for the final pressure and temperature, as for the variable pressures and temperature p_k and T in the integral. Since the integral represents a change of potential its value is *independent of the path of integration*.

Finally we assume that T is the temperature of the primary cell mixture, and that the pure substance k at the temperature T and pressure p_k is in thermodynamic equilibrium when made to communi-

cate with the mixture through a semipermeable membrane. By definition this pressure p_k will be called the *partial pressure* of substance k in the mixture. We may then inject the fluid reversibly through the semipermeable membrane into the primary cell by moving the piston of the auxiliary cell. The work done by the piston is

$$dW_{\rm III} = \frac{p_k}{\rho_k} dm_k \tag{4.5}$$

In this third step the primary and auxiliary cells together constitute a closed system. To evaluate the increase of collective potential in this third step which is reversible we may again apply equation (3.9). No heat being supplied we put ds = 0. Hence the increase of collective potential is

$$d\mathbf{V}_{\mathrm{III}} = d\mathbf{W}_{\mathrm{III}} = \frac{p_k}{\rho_k} dm_k \tag{4.6}$$

The total increase of collective potential V' due to the reversible injection of a mass dm_k into the primary cell by the three foregoing steps is

$$d\mathbf{V}' = d\mathbf{V}_{\mathrm{I}} + d\mathbf{V}_{\mathrm{II}} + d\mathbf{W}_{\mathrm{III}} \tag{4.7}$$

This may be written

$$d\mathbf{V}' = \psi_k dm_k \tag{4.8}$$

where

$$\psi_{k} = \int_{p_{o}T_{o}}^{p_{k}T} \left(\frac{dp_{k}}{\rho_{k}} + \theta d\bar{s}_{k} \right)$$
(4.9)

We shall call this expression the *thermobaric potential* of substance k. Its value is independent of the path of integration. It constitutes a new concept.

The transfer of a mass from the supply cell to the primary cell by the foregoing reversible process will be called a *thermobaric transfer*.

A convenient evaluation of ψ_k is obtained by choosing a path of integration first at constant temperature $T_o(\theta = 0)$ from the pressure p_o to p_k then at constant pressure p_k from the temperature T_o to T. We obtain

$$\psi_{k} = \int_{p_{o}}^{p_{k}} \frac{dp_{k}}{\rho_{k}} + \int_{o}^{\theta} \frac{\bar{c}_{kp}\theta}{T} d\theta$$
(4.10)

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In this expression ρ_k is a function of p_k at the constant temperature T_o and \bar{c}_{kp} is the specific heat per unit mass at constant pressure p_k and variable temperature T.

It should be pointed out that the definition (4.9) of the thermobaric potential is expressed in a form suitable for fluid components. However this is not essential since ψ_k may be defined *physically* as the reversible work required to transfer a unit mass of species k from its supply reservoir to the primary cell. This becomes evident by applying equation (3.6) to the collective system. We may write

$$\psi_k dm_k = d\mathbf{V}' = [\mathbf{W}_k + \mathbf{W}_{\mathbf{H}k}] dm_k \tag{4.11}$$

Where

$$W_{Hk} = \int_{p_o T_o}^{p_k T} \theta d\bar{s}_k$$
(4.12)

is the work accomplished by heat pumps, and W_k is the work accomplished by all other forces.

Hence the thermobaric potential

$$\psi_k = W_k + W_{Hk} \tag{4.13}$$

is the total energy required for the thermobaric transfer of a unit mass.

At this point it is important to introduce the generalized concept of *open potential* of the cell by defining it as the collective potential of the system *constituted by the cell and its supply cells*. When dealing with open cells it will therefore be understood that the term open potential denoted by \mathscr{V} implies the generalized potential. We therefore write

$$d\mathscr{V} = d\mathbf{V}' = \psi_k dm_k \tag{4.14}$$

The justification for this generalization is due to the fact that the thermodynamic state of the collective system is entirely defined by those which define the state of the primary cell, since the masses acquired by the cell are the same as those lost by the supply cells. Further clarification on this point is provided in the next section.

When several pure substances are supplied simultaneously to the cell, assuming it is rigid (no change of volume) and that no heat is supplied directly to the cell, its increase of potential is

$$d\mathscr{V} = \sum_{k=1}^{k} \psi_k dm_k \tag{4.15}$$

If a certain amount of heat dh is supplied to the cell by conduction, in a reversible manner at the temperature T of the cell, the supplied entropy is

$$ds_{\rm T} = \frac{dh}{\rm T} \tag{4.16}$$

According to equation (3.9) the cell potential is increased by an amount θds_{T} , and $d\mathcal{V}$ becomes

$$d\mathscr{V} = \sum_{k=1}^{k} \psi_{k} dm_{k} + \theta ds_{\mathrm{T}}$$
(4.17)

The term θds_{T} represents the work required by a heat pump to extract heat from the thermal well and inject the amount Tds_{T} into the primary cell. We shall refer to this process as a *thermal transfer*.

Until now we have assumed no change of volume of the cell. Again we apply equation (3.9) with $dW_p = -pdv$ representing the work of the total pressure p acting on the cell due to the volume change dv. Hence $d\mathscr{V}$ becomes

$$d\mathscr{V} = -pdv + \sum^{k} \psi_{k} dm_{k} + \theta ds_{\mathrm{T}}$$
(4.18)

The pressure p assumed here is the one measured for a reversible volume change.

It will be noted that $d\mathscr{V}$ in this form represents the reversible work done by forces acting on the collective system. The term -pdv is the work due to the pressure acting on the primary cell, the terms $\psi_k dm_k$ is the work due to thermaric transfer and θds_T is the heat pump work required in the thermal transfer.

The same additive property (2.2) applies to the generalized open potentials. The collective potential of any number of open cells is

$$\mathbf{V} = \sum_{\alpha}^{k} \mathscr{V}_{\alpha} \tag{4.19}$$

5. Relative and collective entropy

An important distinction must be introduced regarding the definition of entropy of an open cell. We shall consider the entropy \mathcal{G} of M.A. Biot

the collective system constituted by the primary cell and the supply cells, and refer to \mathscr{S} at the *collective entropy* of the open primary cell. As already pointed out the differential $d\mathscr{V}$ of the open cell potential given by equation (2.3) is the increase of collective potential of the collective system of the primary and supply cells. It corresponds to an increase of collective entropy of the system equal to

$$d\mathscr{S} = \sum_{p_o, \mathbf{T}_o}^{\mathbf{k}} dm_k \int_{p_o, \mathbf{T}_o}^{p_k \mathbf{T}} d\bar{s}_k + ds_{\mathbf{T}}$$
(5.1)

where the first term is the entropy increase due to thermobaric transfer of the masses dm_k while ds_T is due to the heat injected into the primary cell.

We put

$$\bar{s}_k = \int_{p_o T_o}^{p_k T} d\bar{s}_k \tag{5.2}$$

and call it the relative entropy of the pure substance. Hence

$$d\mathscr{S} = \sum^{k} \bar{s}_{k} dm_{k} + ds_{\mathrm{T}}$$
(5.3)

The term $\sum_{k=1}^{\infty} \bar{s}_k dm_k$ represents the increase of collective entropy due to *convection* and ds_T is the contribution due to *conduction*.

Through the use of these definitions it is possible to avoid Gibbs's paradox without recourse to statistical concepts.

The collective entropy may be used as a state variable since it is a function of the temperature T of the primary cell and the masses m_k of the various components in the cell. This is because the increase in the masses m_k in the primary cell determines the masses m_k which remain in the supply cells. The state of the supply cells is thereby determined at the same time.

6. CHEMICAL POTENTIAL. NEW DEFINITION

According to equation (5.1) the value of ds_{T} is

$$ds_{\rm T} = d\mathcal{S} - \sum^{k} \bar{s}_{k} dm_{k} \tag{6.1}$$

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Substitution of this value into equation (4.18) yields

$$d\mathscr{V} = -pdv + \sum_{k=1}^{k} \mu_{k} dm_{k} + \theta d\mathscr{S}$$
(6.2)

where

$$\mu_k = \psi_k - \theta \bar{s}_k \tag{6.3}$$

provides a new chemical potential μ_k different from the classical concept. Note that it is defined entirely *in terms of the properties of the pure* substance and its partial pressure p_k of equilibrium with the mixture at its temperature T through a semipermeable membrane.

If the state variables of the cell are chosen to be v, m_k and \mathscr{S} equation (6.2) implies

$$\frac{\partial \mathscr{V}}{\partial v} = -p$$

$$\frac{\partial \mathscr{V}}{\partial \mathscr{P}} = \theta$$

$$\frac{\partial \mathscr{V}}{\partial m_k} = \mu_k$$
(6.4)

Note that the third of equations (6.4) is not used to define μ_k but constitutes a new result. This is a consequence of the new definition (6.3) of μ_k and is in contrast with current procedures. Since according to (4.9)

$$d\psi_k = \frac{dp_k}{\rho_k} + \theta d\bar{s}_k \tag{6.5}$$

the differential of μ_k is

$$d\mu_k = \frac{dp_k}{\rho_k} - \tilde{s}_k dT \tag{6.6}$$

This quantity is analogous to Gibbs function except that now the relative entropy \bar{s}_k is a perfectly defined entropy without any arbitrary constant. Equation (6.6) shows that there is no change in μ_k when the substance goes through a *phase change* at constant pressure and temperature.

7. CHEMICAL REACTIONS. NEW EXPRESSIONS FOR THE AFFINITY AND THE HEAT OF REACTION

The foregoing analysis assumes that the substances composing the mixture in the open cell do not react chemically.

If a chemical reaction occurs the analysis must be completed as follows. We shall first consider a closed cell. The mass variations of the various components due to the chemical reaction are written.

$$dm_k = v_k d\xi \tag{7.1}$$

where ξ is the reaction coordinate. If some of the substances do not participate in the reaction the corresponding values of v_k are zero. Conservation of mass requires

$$\sum_{k=0}^{k} v_k = 0 \tag{7.2}$$

The values of v_k are also frequently written as

$$v_k = v'_k \mathcal{M}_k \tag{7.3}$$

where \mathcal{M}_k are the molecular masses and v'_k are called the *stoichiometric* coefficients of the reaction.

For convenience we call dm_k the masses produced by the reaction, positive values of v_k corresponding to substances actually created, while negative values v_k represent substances dissapearing in the reaction.

If a chemical reaction $d\xi$ occurs the cell potential varies by an amount

$$d\mathscr{V}_{ch} = dU_{ch} - T_o d\mathscr{G}_{ch}$$
(7.4)

The cell is assumed rigid and adiabatic.

Hence there is no change in internal energy

$$d\mathbf{U}_{ch} = 0 \tag{7.5}$$

As a consequence

$$d\mathscr{V}_{ch} = -\mathrm{T}_o d\mathscr{G}_{ch} \tag{7.6}$$

where $d\mathscr{G}_{ch}$ is the entropy produced by the reaction. While a statistical definition of $d\mathscr{G}_{ch}$ is implicit in this case, explicit use of statistical concepts will be avoided in its evaluation. Chemical equilibrium corresponds to $d\mathscr{G}_{ch} = 0$.

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We now assume that after the reaction $d\xi$ has occured the cell is open and may receive heat, but remains rigid. If masses dM^k are injected by thermobaric transfer and an entropy ds_T is supplied by thermal transfer the open potential of the cell increases by an amount given by (4.17) i.e.

$$d\mathscr{V}' = \sum_{k=1}^{k} \psi_{k} d\mathbf{M}^{k} + \theta ds_{\mathrm{T}}$$
(7.7)

The total increase of open potential is

$$d\mathscr{V} = d\mathscr{V}_{ch} + d\mathscr{V}' \tag{7.8}$$

or

$$d\mathscr{V} = -\mathrm{T}_{o}d\mathscr{S}_{ch} + \sum_{k}^{k}\psi_{k}d\mathrm{M}^{k} + \theta ds_{\mathrm{T}}$$
(7.9)

The increase of collective entropy $d\mathcal{S}$ is obtained by adding $d\mathcal{S}_{ch}$ to the value (5.3). Hence

$$d\mathscr{G} = d\mathscr{G}_{ch} + \sum_{k=1}^{k} \bar{s}_{k} d\mathbf{M}_{k} + ds_{\mathrm{T}}$$
(7.10)

Elimination of ds_{T} between equations (7.9) and (7.10) yields

$$d\mathscr{V} = -\mathrm{T}d\mathscr{G}_{ch} + \sum_{k=1}^{k} \mu_{k} d\mathbf{M}^{k} + \theta d\mathscr{G}$$
(7.11)

We put

$$\frac{A}{T} = \frac{d\mathscr{G}_{ch}}{d\xi}$$
(7.12)

Hence

$$d\mathscr{V} = -\mathrm{A}d\xi + \sum_{k=1}^{k} \mu_{k}d\mathrm{M}^{k} + \theta d\mathscr{S}$$
(7.13)

The quantity A defined by equation (7.12) coincides with the affinity introduced by De Donder [3]. Simple considerations show that the variables ξ , M^k and \mathscr{S} completely define the state of the collective system for a given choice of initial conditions and supply cells since they determine the composition and temperature of each cell.

When several reactions occur we write

$$d\mathscr{V} = -\sum_{\rho}^{\rho} A_{\rho} d\xi_{\rho} + \sum_{\mu}^{k} \mu_{k} dM_{k} + \theta d\mathscr{S}$$
(7.14)

where A_p and ξ_p are the affinities and the coordinates of the various reactions.

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The concepts of thermobaric and thermal transfers lead to new expressions for the affinity and the heat of reaction which we shall now derive. We assume that when a single reaction occurs in the primary cell we remove the products of the reaction hence

$$d\mathbf{M}_k = -\mathbf{v}_k d\xi \tag{7.15}$$

Note that the "removal" is algebraic since v_k may be positive or negative. Also we maintain the temperature T constant by supplying the required heat. The composition and temperature of the cell do not vary hence the pressure of the mixture is also constant. Therefore we may write

$$ds_{\rm T} = \frac{h_{p\rm T}}{\rm T} d\xi \tag{7.16}$$

where \bar{h}_{pT} is the heat of reaction (positive when endothermic) at constant pressure and temperature with removal of the products of reaction. The usual heat of reaction at constant pressure and temperature is

$$h_{pT} = \bar{h}_{pT} + \sum_{k=1}^{k} v_k h_{pT}^k$$
(7.17)

where h_{pT}^k is the heat of mixture i.e. the heat absorbed by the mixture when a unit mass of substance k is injected reversibly at constant pressure and temperature into the mixture.

Note that \bar{h}_{pT} is more representative of the true chemical energy since it does not contain the additional energy due to mixing. For a perfect gas the heat of mixing vanishes and

$$h_{p\mathrm{T}} = \bar{h}_{p\mathrm{T}} \tag{7.18}$$

During the process just described the variation of collective entropy of the system constituted by the primary cells and the supply cells is obtained from (7.10) introducing the values (7.12) (7.15) and (7.16). This variation of collective entropy is

$$d\mathscr{S} = \left(\underbrace{+\mathbf{A}}_{\overset{\frown}{\mathcal{F}}} \sum^{k} v_{k} \bar{s}_{k} + \frac{\bar{h}_{pT}}{T} \right) d\xi$$
(7.19)

We also consider a *reference cell* of affinity A' temperature T', pressure p' partial pressures p'_k of the reactants and heat of reaction $\bar{h}'_{p'T'}$.

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We assume that in the reference cell a backward reaction $(-d\xi)$ occurs. The change of collective of entropy $d\mathscr{G}_r$ of this reference cell is obtained from (7.19) by substituting the corresponding values of the variables. We obtain

$$d\mathscr{S}_{r} = -\left(\underbrace{\not = A'}_{\neq} \overleftarrow{\not =}^{k} v_{k} \overrightarrow{s}_{k}' + \frac{\overline{h}_{p'T'}}{T'} \right) d\xi \qquad (7.20)$$

where

$$\bar{s}'_{k} = \int_{p_{o}T_{o}}^{p' \kappa T'} d\bar{s}_{k}$$
(7.21)

When the forward and backward reactions occur simultaneously the state of he supply cells does not change since no matter is supplied. At the same time the state of he primary cells does not change. Hence the total entropy S of the collective system remains constant and we may write

$$d\mathbf{S} = d\mathcal{G} + d\mathcal{G}_r = \mathbf{0}$$

Substituting the values (7.19) and (7.20) we derive

$$\underline{A} - \underline{A'}_{\overline{\mathcal{T}}} = \sum_{p'_{k}T'}^{k} d\bar{s}_{k} \stackrel{\overline{\mathcal{T}}}{\neq} \frac{h_{pT}}{T} + \frac{h'_{p'T'}}{T'}$$
(7.22)

If the reference cell is assumed to be in chemical equilibrium, A' = 0 and

$$A = \sum_{p'k}^{k} v_{k} \int_{p'kT'}^{p_{k}T} d\bar{s}_{k} + \frac{\bar{h}_{pT}}{T} - \frac{\bar{h}'_{p'T'}}{T'}$$
(7.23)

This result which is different from the one derived in standard textbooks [4] expresses the affinity in terms of purely calorimetric measurements for the pure substances proviced we know the partial pressures p_k and p'_k of the reactants in the mixture.

Another important result involving the heat of reaction is obtained by considering the change of internal energy of the collective system. For the primary cell this change is

$$d\mathbf{U} = -d\xi \sum_{p_o \mathbf{T}_o}^{k} v_k \int_{p_o \mathbf{T}_o}^{p_k \mathbf{T}} \left(\frac{dp_k}{\rho_k} + \mathbf{T} d\bar{s}_k \right) + \bar{h}_{p\mathbf{T}} d\xi$$
(7.24)

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The first term in the integral is the work done on system and the remainder is the heat provided. Similarly for the reference cell the increase of collective internal energy is

$$d\mathbf{U}_{r} = d\xi \sum_{p, \mathbf{T}_{o}}^{k} \bigvee_{p_{o} \mathbf{T}_{o}}^{p'_{k} \mathbf{T}} \left(\frac{dp_{k}}{\rho_{k}} + \mathbf{T} d\bar{s}_{k} \right) - \bar{h}_{p' \mathbf{T}'}' d\xi$$
(7.25)

Since the state of all cells remains the same the total change of internal energy dU is zero, hence

$$d\mathbf{U} + d\mathbf{U}_r = 0 \tag{7.26}$$

Substitution of the values (7.24) and (7.25) yields.

$$\bar{h}_{p\mathrm{T}} - \bar{h}'_{p'\mathrm{T}'} = \sum^{k} v_{k} \int_{p'_{k}\mathrm{T}'}^{p_{k}\mathrm{T}} \left(\frac{dp_{k}}{\rho_{k}} + \mathrm{T}d\bar{s}_{k}\right)$$
(7.27)

This result which expresses the heat of reaction in terms of mechanical and calorimetric measurements for the pure substances is more general than the classical Kirchhoff relation [4]. The path of integration is arbitrary.

8. REACTING MIXTURE OF PERFECT GASSES

For perfect gasses the heat of mixture vanishes. Hence with $h_{pT}^k = 0$ equaion (7.17) becomes

$$h_{pT} = \bar{h}_{pT} \quad h'_{p'T'} = \bar{h}'_{p'T'}$$
(8.1)

The heat of reaction is the same whether we remove or not the products of reaction. The equation of state is

$$p_k = \rho_k \frac{\mathbf{R}}{\mathcal{M}_k} \mathbf{T}$$
(8.2)

where \mathcal{M}_k is the molecular weight and R the universal gas molar constant. The entropy differential is

$$d\bar{s}_{k} = \frac{1}{\mathcal{M}_{k}} \left[c_{kp}(T) \frac{dT}{T} - R \frac{dp_{k}}{p_{k}} \right]$$
(8.3)

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where $c_{kp}(T)$ is the molar specific heat of the gas at constant pressure. Combining equations (8.2) and (8.3) we obtain

$$\frac{dp_k}{\rho_k} + \mathrm{T}d\bar{s}_k = \frac{c_{kp}(\mathrm{T})}{\mathrm{T}}d\mathrm{T}$$
(8.4)

With this value and (8.1) relation (7.27) becomes

$$h_{pT} - h'_{p'T'} = \sum_{k=1}^{k} v'_{k} \int_{T'}^{T} c_{kp}(T) dT$$
 (8.5)

where $v'_k = v_k / \mathcal{M}_k$ are the stoichiometric coefficients. Equation (8.5) coincides with the classical *Kirchhoff relation* when applied to perfect gasses. If we substitute into equation (7.23) the value (8.3) of $d\bar{s}_k$ and the value h_{pT} derived from (8.5) we obtain for the affinity

$$A = RT \log \frac{K(T)}{p_1^{\nu'_1} p_2^{\nu'_2} \dots p_k^{\nu'_k}}$$
(8.6)

where K(T) is defined by the relation

$$\operatorname{RT}\log K(T) = -\sum_{k}^{k} v_{k}' \int_{T'}^{T} c_{kp}(T) dT + T \sum_{k}^{k} v_{k}' \int_{T'}^{T} \frac{c_{kp}(T) dT}{T}$$
$$+ \operatorname{RT}\sum_{k}^{k} v_{k}' \log p_{k}' + \left(\frac{T}{T'} - 1\right) h_{p'T'}' \qquad (8.7) \quad X$$

For a given reference cell this is only a function of T. At chemical equilibrium A = 0 and (8.6) becomes

$$p_1^{\nu'_1} p_2^{\nu'_2} \dots p_k^{\nu'_k} = \mathbf{K}(\mathbf{T})$$
(8.8)

For a mixture of perfect gasses the partial pressures are

$$p_k = p\gamma_k \tag{8.9}$$

where p is the total pressure of the mixture and γ_k are the molar fractions. Hence equation (8.8) is written

$$p^{-\nu'} K(T) = \gamma_1^{\nu'_1} \gamma_2^{\nu'_2} \dots \gamma_k^{\nu'_k}$$
(8.10)

where $v' = \sum_{k=1}^{n} v'_{k}$. This equation expresses the law of *Guldberg and Waage* for chemical equilibrium and K(T) is the equilibrium constant.

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