COMMENTS ON GIBBS' EQUATION:

The Condition For Chemical Equilibrium In Open Systems*

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The first law of thermodynamics establishes the existence of the internal energy E, a state function, for a closed system. Assume that E exists and is a state function for open systems also. Define q to be the heat transferred to the system due to a temperature gradient, and w to be the work done by the system in addition to that required to introduce or remove material at the boundary. Neglecting kinetic and potential energy changes, the first law for an open system becomes

$$dE = \delta q - \delta w + \sum_{k=1}^{s} \overline{H}_k^{(e)} dn_k^{(e)}, \qquad (1)$$

where δ is a variation operator used to indicate that q and w are not state variables, but are path-dependent functions instead, and where $H_k^{(e)}$ is the partial molal enthalpy of species k (of s species present) entering or leaving the system, and includes the work required to transfer material across the boundary. If the only work done by the system is expansion work, it follows that

$$\delta w + \delta D_v = PdV, \qquad (2)$$

where δD_v is the differential of viscous dissipation of energy. Here dD_v/dt, i.e. the time derivative, is the same quantity as denoted by E_v by Bird *et al.* [1].

For an open system, the second law of thermodynamics may be written

$$TdS = \delta q + TdS_{irr}^{(i)} + TdS^{(e)}, \qquad (3)$$

where $dS_{irr}^{(i)}$ and $dS^{(e)}$ are internal and external contributions to the differential change in the entropy of the system, due to irreversible chemical reaction and viscous dissipation, and to material entering or leaving under different conditions than in the system. Assuming that a state function S, established for closed systems, also exists for open systems, dS is a perfect differential. The internal entropy generation term $dS_{irr}^{(i)}$ must be positive.

In an open system, the differential extent $d\xi$ of a single chemical reaction is defined by

$$dn_k = \nu_k d\xi + dn_k^{(e)}, \qquad (4)$$

where dn_k is the differential change in the number of moles of species k crossing the boundary of the system. Write

$$Tds_{irr}^{(i)} = Ad\xi + \delta D_v \qquad (5)$$

where **A** is called the affinity of the reaction. In the absence of viscous dissipation, eq. (5) is essentially a defining relationship for the affinity **A**.

Define *chemical equilibrium* by the vanishing of the chemical reaction part of $dS_{irr}^{(i)}$, independent of the existence of irreversibilities introduced by viscous dissipation or by material entering or leaving the system. Then

$$Ad\xi = 0 \qquad \text{[eq], (6)}$$

where [eq] indicates constraint to paths of chemical equilibrium. Since the variation $d\xi$ is arbitrary, the necessary and sufficient condition for chemical equilibrium becomes

$$A = 0 \qquad \text{[eq], (7)}$$

which means that the driving force for the reaction is zero. If $A \neq 0$ even though no reaction occurs ($d\xi = 0$), the system is not at stable equilibrium. For example, a mixture of hydrogen and oxygen at room temperature does not react at any measurable rate, but may be made to do so by

introducing a spark or a suitable catalyst, such as spongy platinum. The spontaneous reaction is highly irreversible, showing that $dS_{irr}^{(i)}$, is positive or, from Eq. (5), that $A \neq 0$. The unreactive mixture is not at true chemical equilibrium, but its state has been termed "false equilibrium" [2] or "metastable equilibrium" [3].

Substituting Eqs. (1), (2), (3), and (5) into the differential of Gibbs energy,

$$dG = dE + PdV + VdP - TdS - SdT, \quad (8)$$

we obtain

$$dG = -SdT + VdP - Ad\xi + \sum_{k=1}^{s} \overline{H}_k^{(e)} dn_k^{(e)}$$

$$- TdS^{(e)}, \quad (9)$$

which may be considered as a form of Gibbs' equation for open systems in the absence of external force fields [2]. Since $ds^{(e)}$ depends on material crossing the boundary, and vanishes for $dn_k^{(e)} = 0$ $(k = 1, 2, \ldots, s)$, we have immediately

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{T,P,n^{(e)}}, \quad (10)$$

where the subscript $n^{(e)}$ indicates that the differentiation is performed under the constraint of no
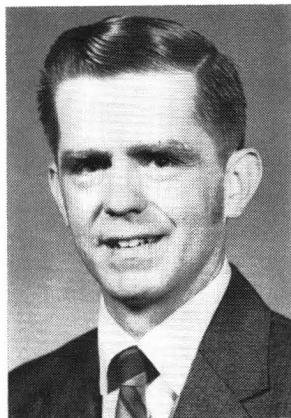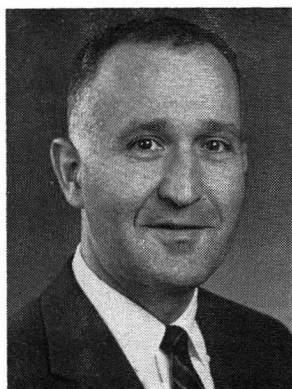
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A general condition of chemical equilibrium for open systems is derived . . . with the condition of chemical equilibrium defined in Eq. 6, a restriction to constant temperature and pressure is unnecessary.

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material crossing the boundary. Hence the affinity of a chemical reaction in an open system is the same as that in a closed system. Considering the Gibbs energy G to be a function of temperature, pressure, and the numbers of moles of all species present, Eq. (10) becomes

$$A = -\sum_{k=1}^{s} \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_1} \left(\frac{\partial n_k}{\partial \xi}\right)_{T,P,n^{(e)}}$$

$$= -\sum_{k=1}^{s} \nu_k \mu_k \quad (11)$$

with the use of Eq. (4). The chemical potential μ_k of species k is defined by

$$\mu_k = \left(\frac{\partial G}{\partial n_k}\right)_{T,P,n_1}, \quad (12)$$

where the subscript n_1 means that the number of moles of each species except species k is held constant. Invoking the principle of microscopic reversibility (Tolman) [4], each reaction in a multiple-reaction system at chemical equilibrium must be independently in equilibrium. Therefore, from Eqs. (7) and (11), it follows that

$$\sum_{k=1}^{s} \nu_{ik} \mu_k = 0 \; (i = 1, 2, \ldots, r) \; [eq], \quad (13)$$

which is the condition of chemical equilibrium, valid for open systems.

Using a different derivation, a number of authors, including Hougen [5], Lewis and Randall, [6], Moore [7], Van Ness [8], Aris [9], Waser [10], and Luder [11], imply that Eq. (13), or its equivalent, holds as the condition for chemical equilibrium only at constant temperature and pressure, and fail to indicate its generality. From the above development, with the condition of chemical equilibrium defined by Eq. (6), a restriction to constant temperature and pressure or to any other set of constraints is unnecessary. Since the chemical potentials are intensive variables, they possess a value at every point in a system;

hence, chemical equilibrium exists at any point for which Eq. (13) holds. In fact, Eq. (13) is valid as the condition of chemical equilibrium for *arbitrary* thermal and mechanical variations in an open system.

Further information can now be obtained regarding the nature of $dS^{(e)}$, the contribution to dS due to material crossing the boundary. The usual form of Gibbs' equation for open systems (Prigogine and Defay [2]) is

$$dG = -SdT + VdP + \sum_{k=1}^{s} \mu_k dn_k. \qquad (14)$$

Equating two expressions for dG, from Eqs. (9) and (14), we have

$$\sum_{k=1}^{s} \mu_k dn_k = -Ad\xi + \sum_{k=1}^{s} \overline{H}_k^{(e)} dn_k^{(e)} - TdS^{(e)}. \qquad (15)$$

Substitution from Eqs. (4) and (11) results in

$$TdS^{(e)} = \sum_{k=1}^{s} [\overline{H}_k^{(e)} - \mu_k] dn_k^{(e)} \qquad (16)$$

Now

$$\mu_k = \overline{H}_k - T\overline{S}_k, \qquad (17)$$

and

$$\mu_k^{(e)} = \overline{H}_k^{(e)} - T^{(e)}\overline{S}_k^{(e)} \qquad (18)$$

where $\mu_k^{(e)}$ and $\overline{S}_k^{(e)}$ are the chemical potential and partial molal entropy, respectively, of species k crossing the boundary, and $T^{(e)}$ is the temperature of the material crossing the boundary. Hence, Eq. (16) becomes

$$TdS^{(e)} = T\sum_{k=1}^{s} \overline{S}_k dn_k^{(e)} + \sum_{k=1}^{s} [\overline{H}_k^{(e)} - \overline{H}_k] dn_k^{(e)} \qquad (19)$$

$$= T^{(e)}\sum_{k=1}^{s} \overline{S}_k^{(e)} dn_k^{(e)} + \sum_{k=1}^{s} [\mu_k^{(e)} - \mu_k] dn_k^{(e)}.$$

Therefore $dS^{(e)}$ includes a term to account for the differences between either partial molal enthalpies or chemical potentials of the species crossing the boundary and those in the system, depending on whether the partial molal entropy terms are described in terms of properties of the system or of properties of the material crossing the boundary.

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Nomenclature

A = Affinity of a chemical reaction
D_v = Viscous dissipation of energy
E = Total internal energy
G = Total Gibbs energy, $H - TS$
H = Total enthalpy
n_k = Number of moles of species k
P = Pressure
q = Heat transferred to the system due to a temperature gradient
S = Total entropy
s = Number of species in the system
T = Absolute temperature
V = Total volume
w = Work done by the system

Greek Symbols

δ = Variation operator
μ_k = Chemical potential of species k
ν_{ik} = Stoichiometric coefficients of species k in reaction i
ξ = Extent of chemical reaction

Superscripts and Subscripts

— = Partial molal quantity
(e) = Material crossing the boundary
(i) = Material in the system
i = Chemical reaction
irr = Irreversible process
k = Species of material
$n^{(e)}$ = Differentiation performed under constraint of no material crossing the boundary