Equilibrium Thermodynamics of Chemical Reaction Coupled with Other Interfacial Reactions Such as Charge Transfer by Electron, Colligative Dissolution and Fine Dispersion: A Focus on Distinction between Chemical and Electrochemical Equilibria

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Abstract : This article involves a unified treatment of equilibrium thermodynamics of the chemical reaction coupled with other interfacial (phase boundary) reactions. The modified (restrictive) chemical potential μ_k^+, such as electrochemical potential, hydrostatic-chemical (mechanochemical) potential (exceptionally in the presence of the pressure difference) and surface-chemical potential, was first introduced under the isothermal and isobaric conditions. This article then enlightened the equilibrium conditions in case where the release of chemical energy is counterbalanced by the supply of electrical energy, by the supply of hydrostatic work (exceptionally in the presence of Δp), and finally by the release of surface energy, respectively, at constant temperature T and pressure p in terms of the modified chemical potential μ_k^+. Finally, this paper focussed on the difference between chemical and electrochemical equilibria based upon the fundamentals of the isothermal and isobaric equilibrium conditions described above.

Keywords : Modified (restrictive) chemical potential, Hydrostatic-chemical (mechanochemical) potential, Surface-chemical potential, Electrochemical potential, Modified (restrictive) Gibbs free energy

1. Introduction

In order to enter the theme of this article, we start raising a question which one a higher rank concept is, electrochemical equilibrium or chemical equilibrium. Is chemical equilibrium really a lower rank concept, because emf becomes zero in value under its equilibrium condition? The answer is definitely untrue. In this place, we restricted electrochemical equilibrium to charge transfer by electron which is regarded as the electrochemical system. We took in particular membrane equilibrium out of account.

Chemical equilibrium is attained as a result of transfer of the chemical potential (energy), *i.e.* transfer of the mass of all chemical species within the system, which is achieved in "the absence of electrical constraint"[1]. In contrast, electrochemical equilibrium is

established as a consequence of transfer of the chemical potential (energy) coupled with a useful electrical potential (energy), *i.e.* transfer of electrical charge of electrons within the system, which is achieved in "the presence of electrical constraint"[1].

The ambiguous interpretation of this problem even in the relevant textbook[2-4] sometimes motivates the authors to write a summary paper on the integrative concept of equilibrium thermodynamics of all the mixed-chemical and other interfacial (phase boundary) reactions, in an attempt to quench the graduate students' or researchers' thirsts for knowledge.

In the present article, the modified (restrictive) chemical potential μ_k^+ was first derived from the modified (restrictive) Gibbs free energy ΔG^+ being regarded as the maximum useful (electrical, hydrostatic and surfacial) work at constant temperature T and presses p. Then the isothermal and isobaric equilibrium conditions for the chemical reaction

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coupled with the respective phase boundary (inter-facial) reactions were given. Finally, clear distinction between chemical and electrochemical equilibria was made based upon the fundamentals of the isothermal and isobaric equilibrium conditions discussed above.

2. Integrative Concept of Modified (Restrictive) Chemical Potential μ_k^+

Let us first consider the chemical potential when a chemical reaction purely occurs at constant temperature T and pressure p. In order to derive the condition for chemical equilibrium, it is very convenient to introduce the chemical potential of the kth chemical species μ_k under the isothermal and isobaric conditions during the chemical reaction in terms of Gibbs free energy G or alternatively of internal energy U as follows:

$$\mu_k = \left(\frac{\partial G}{\partial n_k}\right)_{T, p, n_j \neq n_k} \qquad (1)$$

or alternatively

$$\mu_k = \left(\frac{\partial U}{\partial n_k}\right)_{S, V, n_j \neq n_k} \qquad (1a)$$

where n is the number of moles, k and j mean solvent and solute, sometimes the kth solute and the jth solute, or the kth phase and the jth phase, respectively, S and V represent entropy and volume, respectively.

The definition (1a) is physically clear and unique, but it makes sometimes inconvenient because it is experimentally difficult to fix the entropy in value[5] and also constant variables of S and V outside the partial differential are not both intensive. In contrast, the definition (1) is conveniently employed in the experimental and theoretical approaches to equilibrium thermodynamics at materials system[5] because the natural variables T and p for G are both intensive.

Secondly, we come to the definition of the electrochemical potential of the kth species $\mu_k^+(q)$[5-9] when the chemical reaction is superimposed on the charge transfer reaction (electron exchange reaction) at constant T and p. As a result of this superimposition, dG is given by

$$dG = -SdT + Vdp + \gamma dA + Edq + \sum_{k=1}^{k} \mu_k dn_k \qquad (2)$$

where E is the electrode potential or emf and q is in general the charge of the charged species.

During the isothermal and isobaric processes, dG reduces to

$$(dG)_{T, p} = \sum_{k=1}^{k} \mu_k dn_k + E \sum_{k=1}^{k} \left(\frac{\partial q}{\partial n_k}\right)_{T, p, n_j \neq n_k} dn_k$$

$$= \sum_{k=1}^{k} \left[\mu_k + E\left(\frac{\partial q}{\partial n_k}\right)_{T, p, n_j \neq n_k}\right] dn_k \qquad (2a)$$

From Eq. (2a) we define the electrochemical potential of the kth oxidised (reduced) species μ_k^{+}[6-8] as

$$\mu_k^+(z) = \mu_k + z_k FE^{\alpha} \qquad (3)$$

where z_k is specifically the charge of the kth oxidised (reduced) species, F the Faraday constant ($96,500$ C mol^{-1}), and α is the phase.

Thirdly, we consider the case when the chemical potential decrease is accompanied by a spontaneous development of hydrostatic pressure Δp at constant T. As a result of the combined chemical potential drop and generated hydrostatic pressure, dG is given by

$$dG = -SdT + Vdp + \sum_{dk=1}^{k} \mu_k dn_k \qquad (4)$$

At constant T, dG reduces to

$$(dG)_T = \sum_{k=1}^{k} \mu_k dn_k + \Delta p \sum_{k=1}^{k} \left(\frac{\partial V}{\partial n_k}\right)_{n_j \neq n_k} dn_k$$

$$= \sum_{k=1}^{k} [\mu_k(\Delta p = 0) + \Delta p \bar{V}_{m, k}] dn_k \qquad (4a)$$

Similarly, from Eq. (4a) we define the hydrostatic-chemical (mechanochemical) potential $\mu_k^+(p)$[9]

$$\mu_k^+(p) = \mu_k(\Delta p = 0) + (\Delta p \bar{V}_{m, k}) \qquad (5)$$

The definition of the hydrostatic-chemical potential $\mu_k^+(p)$ can be easily transposed to that of the gravitational chemical potential by replacing the term $\Delta p \bar{V}_{m, k}$ in Eq. (5) with $M_k g \Delta \bar{h}$, where M_k is the mole mass of the kth species, g the gravitational acceleration, and $\Delta \bar{h}$ is the height (altitude) difference.

Finally, we come to the case when the chemical potential increase is accompanied by development

of surface energy at constant T and p. As a result of this superimposition of the chemical potential increased and surface energy developed by fine dispersion of the system, dG is given by

$$dG = -SdT + Vdp + \gamma dA + \sum_{k=1}^{k} \mu_k dn_k \qquad (6)$$

At constant T and p, dG reduces to

$$(dG)_{T,p} = \sum_{k=1}^{k} \mu_k dn_k + \gamma \sum_{k=1}^{k} \left(\frac{\partial A}{\partial n_k} \right)_{T,p,\,n_j \neq n_k} dn_k$$

$$= \sum_{k=1}^{k} \left[\mu_k + \gamma \sum_{k=1}^{k} \left(\frac{\partial A}{\partial n_k} \right)_{T,p,\,n_j \neq n_k} dn_k \right] dn_k \qquad (6a)$$

Similarly, from Eq. (6a) we define the surface-chemical potential $\mu_k^+(A)$[10]

$$\eta_k^+(A) = \mu_k + \gamma \sum_{k=1}^{k} \left(\frac{\partial A}{\partial n_k} \right)_{T,p,\,n_j \neq n_k} \qquad (7)$$

where A is the surface area. Table 1 summarises the modified (restrictive) chemical potential μ_k^{+} [10].

3. Isothermal and Isobaric Equilibrium Conditions for the Chemical Reaction Coupled with Other Interfacial Reactions

One gives criteria for spontaneity (irreversibility) and chemical equilibrium under the isothermal and isobaric conditions in the absence of any constraints as follows:

$$(dG)_{T,p} = \sum_k \mu_k dn_k = \delta W_{max}(useful) = -A_F \gtrless 0 \qquad (8)$$

where one inequality > 0 means the endergonic reaction (greek, work consuming), forced forward reaction, $i.e.$ spontaneous backward reaction which is historically comparable with the endothermic reaction ($\Delta H > 0$), the equality $= 0$ chemical equilibrium, and another inequality < 0 indicates the exergonic reaction (greek, work producing), spontaneous forward reaction which is historically comparable with the exothermic reaction ($\Delta H < 0$).

$\mu_k = (\partial G / \partial n_k)_{T,p,n_j \neq n_k}$ is defined as the chemical potential (partial molar free energy at constant T and p) increased by the transfer of the kth chemical species (component), n number of mole, ΔG origi-

Table 1. Overview of modified (restrictive) chemical potential for chemical reaction coupled under various kinds of constraints [10]

System	Special form of potential energy	Definition of modified (restrictive) chemical potential
Electrochemical system (heterogeneous system with ions)	Electrical energy	$\mu_k^+ = \eta_k = \mu_k + z_k F(e) \phi^\alpha$ α : phase
Osmotic system	Osmotic pressure	$\mu_k^+ = \mu_k(\Delta p = 0) + \Delta p \overline{V}_{m,k}$ Δp : osmotic pressure $\left(\frac{\partial V}{\partial n_k} \right)_{T,p,\,n_j \neq n_k} = \overline{V}_{m,k}$: partial molar volume of the kth species k: solvent j: solute
Gravitational field	Gravitational potential energy	$\mu_k^+ = \mu_k + M_k g \Delta \overline{h}$ M_k : molecular weight [kg mol^{-1}] $\left(\frac{\partial h}{\partial n_k} \right)_{T,p,\,n_j \neq n_k} = \overline{V}_{m,k}$: partial molar height of the kth species h: phase k or isotope k j: phase j or isotope j
System with small particles (crystallites)	Surface energy	$\mu_k^{+} = \mu_k + \Gamma \left(\frac{\partial A}{\partial n_k} \right)_{T,p,\,n_j \neq n_k}$ $\left(\frac{\partial A}{\partial n_k} \right)_{T,p,\,n_j \neq n_k} = \overline{A}_k$: partial molar interfacial area of the kth species A: interfacial area k: solvent or solute k j: solute j

nally defined as δW (useful) which just represents the maximum useful work obtained during the reversible process at constant T and p, and A_F means the affinity.

Notice that J. Thomsen (1826-1909) and M. Berthelot (1827-1907) once defined $A_F = -\Delta H$, which is nowadays regarded as a wrong concept. It is noted that the terminology endergonic and exergonic is now sometimes used in biochemistry.

First let us consider a more general case of the condition for chemical equilibrium during the isothermal and isobaric processes in the absence of the electrical constraint[1], $\Delta G = 0$ as follows:

$$(dG)_{T,p} = \sum_k \mu_k dn_k = \delta W_{max}(useful) = -A_F = 0 \quad (9)$$

Then let us consider a more specific case that the chemical reaction providing transfer of the mass of the chemical species is coupled (mixed) with or superimposed on other interfacial (phase boundary) reaction producing "internal" useful work, for instance, (a) the system (electron) performs an "internal" electrical work {(-) sign} as a consequence of a charge transfer reaction of the charged particles including electron between two phases with different inner electrical (Galvani) potentials. (b) The system performs an "internal" gravitational work {(-) sign} based upon the altitude change of the particles in a gravitational field.

$$(dG)^+_{T,p} = \sum_k \mu_k dn_k + \sum_k E_{P,k} dn_k \quad (10)$$

where $(dG)^+_{T,p}$ is the modified (restrictive) Gibbs free energy for coupled (composite) reaction at constant T and p, k the neutral chemical species (component) and charged particles including electron, $(dG)_{T,p} = \sum_k \mu_k dn_k$ the chemical work performed by means of the mass transfer of the chemical species, $\mu_k = (\partial G^+/\partial n_k)_{T,p,n_j \neq n_k}$ the partial molar free energy of the kth chemical species at constant T and p increased by the mass transfer of the kth chemical species, $\delta W_{in} = \sum_k E_{P,k} dn_k$ is "internal (inner)" work performed between "internal" particles within the system. By contrast, "external (outer)" work means $-pdV$ (volume expansion) work or simply work done by the system on the surroundings and vice versa, $E_{P,k} = (\partial G^+/\partial n_k)_{T,p,n_j \neq n_k}$ is the partial molar potential energy of the kth chemical species at constant T and p increased by the charge transfer or

other energy transfer of the kth chemical species.

In the latter case of the chemical reaction coupled with other interfacial reaction, "internal (inner)" work is performed on the surroundings as useful work. In general, we define the modified (restrictive) chemical potential as

$$\mu_k^+ = \mu_k + E_{P,k} \quad (11)$$

where $\mu_k^+ = (\partial G^+/\partial n_k)_{T,p,n_j \neq n_k}$ is the special modified (restrictive) chemical potential {(+) sign means a positive additive term}, in other words, it represents the modified (restrictive) partial molar Gibbs free energy at constant T and p increased by both the mass transfer and the charge transfer or other energy transfer of the kth chemical species.

Now we establish the condition for the isothermal and isobaric thermodynamic equilibria of the chemical reaction coupled with other interfacial reaction producing "internal (inner)" useful work (in the presence of modified, $e.g.$ electrical constraint, $\Delta G \neq 0$)[1]

$$\sum_k \mu_k^+ dn_k = 0 \quad \text{(equality)} \quad (12a)$$

$$(dG)_{T,p} = \sum_k \mu_k dn_k = \delta W_{max}(useful) = -A_F \neq 0$$
$$\text{(inequality)} \quad (12b)$$

Now electrochemical equilibria can be exemplified with the following two examples of a half cell and a galvanic cell to evaluate the value of emf E.

Example 1. Let us consider the following half cell α/β, $e.g.$ $Zn(\alpha)/Zn^{2+}(\beta)(ZnCl_2$ solution), where / means the interface (phase boundary). We shed light on a more specific case of half cell equilibrium (13) by employing the first approach

$$Zn \leftrightarrows Zn^{2+} + 2e^\alpha \quad (13)$$

Here, "$\rightarrow$" produces Nernst's dissolution pressure ("Auflösungsdruck") and "$\leftarrow$" generates Nernst's osmotic pressure ("Osmotischer Druck"). Considering the state change of $Zn^\alpha \rightarrow Zn^{2+,\beta}$ (solution phase), we get $\sum v_k \mu_k = (\mu_{Zn^{2+}} - \mu_{Zn}) < 0$. The question is why is the (-) sigh for the chemical potential change. The answer is owing to $c_{Zn^{2+}}$ (initial metal state α) $> c_{Zn^{2+}}$ (final solution state β). Accordingly, "internal" electrical work should be performed during the charge transfer of $Zn^\alpha \rightarrow Zn^{2+,\beta}$

$\delta W_{ele} = 2F(\phi^\beta - \phi^\alpha) > 0$

We know $\phi^\beta(solution) > 0$, $\phi^\alpha(metal) < 0$. At the standard state, we set $\mu^o_{Zn} = 0$ and $\phi^{0,\alpha} < 0$, consequently

$$\mu^o_{Zn^{2+}} < 0 \text{ and } \phi^{0,\alpha} < 0 \tag{14}$$

The alternative approach applies to the same half cell equilibrium. Applying the electrochemical equilibrium condition (electrical constraint)

$$\sum_k v_k \eta_k = 0 \tag{15a}$$

to reaction (13) gives

$$\sum_k v_k \eta_k = (\mu^\beta_{Zn^{2+}} - \mu^\mu_{Zn}) - 2F\phi^\alpha_e$$

$$= \mu^\beta_{Zn^{2+}} - \mu^\alpha_{Zn} + 2F(\phi^\beta_e - \phi^\alpha_e) = 0 \tag{15b}$$

This means that $(\mu^\beta_{Zn^{2+}} - \mu^\alpha_{Zn})$ (*chemical work*) < 0 is compensated by $2F(\phi^\beta_e - \phi^\alpha_e)$ (*electrical work*) > 0 where ϕ^β_e is reference point. It is emphasised that strongly speaking, the second equality sign in Eq. (15b) is not mathematically correct. This compensatory situation is comparable with $\Delta G = \Delta H - T\Delta S = 0$ for the chemical equilibrium condition in view of 2 collaborating contributions of ΔH and ΔS. At the standard state, we set

$\mu^o_{Zn} = 0$ and $\phi^{o,\beta} = 0$, consequently

$$\mu^o_{Zn^{2+}} < 0 \text{ and } \phi^{o,\alpha} < 0 \tag{16}$$

The two methods give the same results of Eqs. (14) and (16) although the view point is somewhat different.

Example 2. Let us go to the 2nd example of the following galvanic cell (2 half cells), *e.g.* Zn^α/ $ZnSO_4^{aq}$//$CuSO_4^{aq}$/Cu^β (Daniell cell). If the overall cell reaction occurs spontaneously, $\sum v_k \mu_k$ = chemical dissolution work < 0 should be satisfied. In other word, the presence of the electrical constraint, $\Delta G \neq 0$ is expressed as $2F(\phi^\alpha_e - \phi^\beta_e) = -(\eta^\alpha_e - \eta^\beta_e) \neq 0$ which just corresponds to Eq. (12b) expressing the inequality. $2F(\phi^\alpha_e - \phi^\beta_e)$ means the electrical work performed by electron (the system) on the galvanic circuit < 0, where α and β are two different electrodes, anode α and cathode β.

Therefore, the chemical dissolution work by the spontaneous cell reaction is counterbalanced by the electrical work performed by electron < 0. In other word, this electrical constraint can be formulated with an equality

$$\sum v_k \eta_k = \sum v_k \eta_k + 2F(\phi^\beta_e - \phi^\alpha_e) = 0 \tag{17}$$

which just corresponds to Eq. (12a), suggesting that the 1st term 'consumption (-) of the chemical energy' is compensated by the 2nd term 'gain (+) of the electrical energy'. Here, $(\phi^\beta_e - \phi^\alpha_e) = emf > 0$ should be hold.

Equilibria of the chemical energy coupled with hydrostatic pressure work spontaneously generated can be exemplified with three examples of osmotic-chemical equilibrium, mechanochemical equilibrium and barometric-chemical equilibrium. Similarly to electrochemical equilibria, osmotic pressure is spontaneously developed from the fact that the decrement in chemical potential by the addition of solute atoms is compensated by the increment of osmotic pressure work.

From the equilibrium constraint $\mu^+_k(p) = 0$, we easily get[9]

$$c_k = c^o_k \exp\left(-\frac{\Delta p \overline{V}_{m,k}}{RT}\right) \tag{18}$$

where c_k is the concentration of the kth species, c^o_k is the concentration of the kth species at the standard state. This means the equilibrium concentration of the mechanically activated species decreases with increasing external pressure Δp which results in spatial localisation [mechanochemical effect (heterogeneity)] of the mechanically activated species (atoms).

When the term $\Delta p \overline{V}_{m,k}$ in Eq. (18) is replaced by $M_k g \Delta \overline{h}$, Eq. (18) reduces to "barometric equation". It is noted that if the gravitational potential $\Delta \overline{h} = (h_2 - h_1)$ were to be enhanced, for example, using a centrifuge, one would intensify the compositional difference $\Delta c_k = (c^1_k - c^2_k)$, noticing that $\Delta \overline{h}$ just has an opposite sign of Δc_k, because the argument of c_k contains the (-) sign.

Assuming a spherical particle phase with radius r and surface energy γ, equilibrium of fine-dispersed materials system can be characterised by

$$(dG)^+_{T,p} = \sum_k \mu_k dn_k + \gamma d\underline{A} = -(\Delta p d\underline{V}) + \gamma d\underline{A} = 0 \tag{19}$$

which gives

$$\Delta p \; = \; \gamma \left(\frac{\partial \underline{A}}{\partial \underline{V}}\right)_{T,p,n_k \neq n_j} \qquad = \gamma \frac{8\pi r\,dr}{4\pi r^2 dr} = \frac{2\gamma}{r} \qquad (19a)$$

where the underline – means the molar quantity. The 1 st term means the decrease in equilibrium pressure by generation of an infinitely large-sized phase {energy consumption (-)} or the 1 st term means the increase in equilibrium pressure by generation of many fine-dispersed phases {energy gain (+)} and the 2nd term represents the increase in surface energy by production of many fine-dispersed phases {energy gain (+)}.

Alternatively we can also calculate the Δp above Eq. (19a)[5] using the surface-chemical potential defined by Eq. (7) and Fig. 1. First let us consider $\eta_{A,k}$ for a droplet in Fig. 1(a) and the flat (compact) liquid in Fig. 1(c)! For a droplet consisting of phase 2, we write

$$\eta^2(r = r) = \mu^2(r = \infty) + \gamma \left(\frac{\partial A}{\partial n}\right)_{p,T}$$

$$\eta^1(r = r) = \mu^1(r = \infty) + RT \ln p^1(r + r)$$
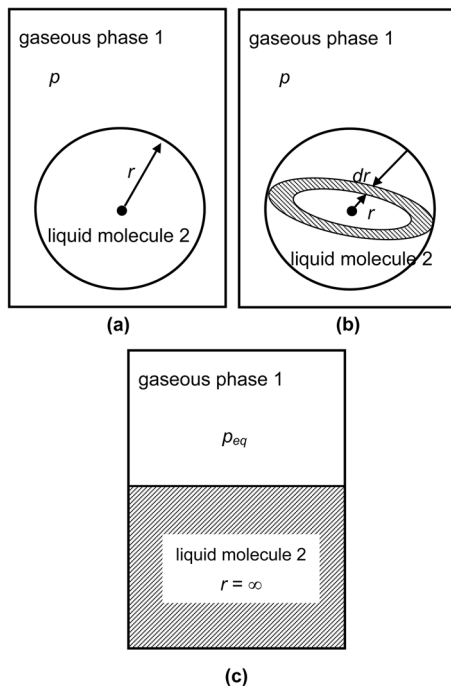
Fig. 1. (a) One spherical molecule (*r*) 2 with a condensed phase in its gaseous phase 1, (b) one spherical molecule (*r* + *dr*) 2 with a condensed phase in its gaseous phase 1, and (c) thermodynamic equilibrium between a bulk liquid phase 2 and its gaseous phase 1.

At equilibrium between a droplet 2 and its gaseous phase 1, the following equality is satisfied

$$\eta^2(r = r) = \eta^1(r = r)$$

It follows

$$\mu^2(r = \infty) + \gamma \left(\frac{\partial A}{\partial n}\right)_{p,T} = \mu^1(r = \infty) + RT \ln p^1(r = r)$$

$$(20a)$$

For the flat (compact) liquid consisting of phase 2, we write $\eta^1(r = \infty) = \mu^1(r = \infty) + RT \ln p^1(r = \infty)$ + no contribution of surface energy

$$\eta^1(r = \infty) = \mu^1(r = \infty) + RT \ln p^1(r = \infty)$$

At equilibrium between the flat (compact) liquid 2 and its gaseous phase 1, the following equalities hold

$$\eta^2(r = \infty) = \eta^1(r = \infty)$$

$$\mu^2(r = \infty) = \mu^1(r = \infty) + RT \ln p^1(r = \infty) \qquad (20b)$$

Performing an operation of subtraction {Eq. (20a) - Eq. (20b)}, we get

$$\gamma \left(\frac{\partial A}{\partial n}\right)_{p,T} = RT \ln \frac{p(r = r)}{p(r = \infty)}$$

since, $\left(dn = \frac{dV}{\underline{V}}\right)$, $\left(\frac{\partial A}{\partial n}\right) = \underline{V} \frac{dA}{dV} = \underline{V} \frac{8\pi r\,dr}{4\pi r^2 dr} = \frac{2\underline{V}}{r}$

If x is very small, $\ln(1 + x) \approx x$, $\ln(1 + x) \approx -x$, $\ln(1 + x) \approx +x$ and $\exp(-x) \approx (1 - x)$. Considering the relations $\Delta p = (p - p_{eq})$ and $\underline{V} = RT$

$$\Delta p \; = \; \frac{2\gamma}{r} \qquad\qquad (qed) \quad (19a)$$

For the water droplet with a radius of 10^{-5} cm, for instance, the overpressure $\Delta p = 14.4$atm results at 20ºC.

Combining Eq. (19) and the Clausius-Clapeyron equation, we get[5]

$$\Delta T_m \; = \; \frac{2\Delta \underline{V}^{s \to l} \gamma_s^l}{\Delta \underline{S}_m r} \qquad\qquad (19b)$$

where ΔT_m is the melting point depression (elevation) by fine dispersion, s the solid phase, l the liquid phase, $s \to l$ the transition of solid to liquid phase,

l/s the interface between solid and its liquid phase, and ΔS_m is the molar melting entropy change. Eq. (19b) which is in particular called Thomson-Frenkel equation and is valid for nano-materials, indicates that as the crystallite grows to the infinite in size r, ΔT_m approaches from (-) or (+) value to zero, depending upon the (-) or (+) sign of molar volume change $\Delta V^{s \rightarrow l}$, respectively. For instance[5] water droplet with a radius of 10^{-2} μm and Au nano-particle with 10^{-2} μm give a negative value -0.048 K and a positive value + 3.78 K, respectively, in ΔT_m.

In the broader sense we count the further systems at which reaction with a negative work done on the surroundings is just coupled with other reaction with a positive useful work obtained, so that for the latter reaction is forced through the spontaneous occurrence of the former reaction. For example, such reactions are of great significance for physiological process where oxidation of glycogen in muscle is expended to perform a negative mechanical work as a consequence or for photosynthesis of carbohydrate in green plant, where both a strong oxidation of H_2O to O_2 under absorption of solar energy and reduction of CO_2 to carbohydrate occur simultaneously.

4. Chemical Equilibrium at $E = 0$ Characterised by Equilibrium Constant K_a (Standard Gibbs Free Energy Change of Chemical Reaction ΔG^o)

From the definition of G at constant T and p, we get

$$(dG)_{T,p} = dH - TdS \tag{21a}$$

$$(dG)_{T,p} = \delta Q_{irr} - TdS \tag{21b}$$

The 2nd law gives an equality $dS = \delta Q_{rev}/T$ and an inequality $dS > \delta Q_{irr}/T$. Here, one subscript rev means the reversible process and another subscript irr is the irreversible process. Therefore, $\delta Q_{irr} < \delta Q_{rev}$. We define the degraded energy lw as

$$lw = \delta Q_{irr} - \delta Q_{rev} = \delta W_{rev} < \delta W_{irr} \leq 0$$

which is regarded as the degree (measure) of irreversibility (spontaneity). This gives extremely 2 limiting cases: $lw = 0$ if completely reversible process to $lw = \delta W_{rev}(max) = -\delta Q_{rev}$.

Finally we write in differential form

$$(dG)_{T,p} = \delta Q_{irr} - \delta Q_{rev} = \delta W_{rev} - \delta W_{irr} < 0 \tag{22a}$$

We find also in definite integral form

$$(\Delta G)_{T,p} = Q_{irr} - Q_{rev} = W_{rev} - W_{irr} < 0 \tag{22b}$$

We will discuss Eq. (22) later along with Eq. (34).

If the irreversible (spontaneous) process (forward reaction) occurs at constant T and p, we get an inequality

$$(\Delta G)_{T,p} < 0 \tag{23a}$$

For a reversible change

$$(\Delta G)_{T,p} = 0 \ (dG = 0, \ G = min) \tag{23b}$$

$$\Delta G = \Delta H - T\Delta S$$

ΔG is composed of two driving forces of ΔH acting as a hot heat (the fire) and ΔS acting as a cold heat or as a degree of randomness or as a minus(-) degree of information (the freezer). It is noted that the 2 driving forces ΔH(min) and ΔS(max) act sometimes in concert, sometimes at variance with each other. ΔG(min) simply acts as an arbiter between two quantities.

From the above, we understand reversibility as follows. When the intensive variables such as pressure p, electrical potential E, surface energy γ are opposed to the external applied variables, we call a reversible process just like a tug-of-war between two evenly matched partners.

Now chemical equilibria can be exemplified with the following three examples of the chemical reaction in the absence of any electrical constraints to evaluate the values of ΔG^o and K_p.

Example 1.

$$H_2^g + \frac{1}{2}O_2^g = H_2O^{aq} \tag{24}$$
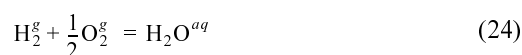
The condition for chemical equilibrium (24) gives

$$\Delta G = W_{max}(useful) = 0 \tag{25}$$

$$\sum v_k \mu_k = 0$$

$$\Delta G^o = \mu_{H_2O}^o - \mu_{H_2}^o - \frac{1}{2}\mu_{O_2}^o = -RT\ln K_p = RT\ln \frac{P_{H_2}P_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \tag{26}$$

where the superscript ^{o} designates the standard state ($a_k = 1$, $p_k = 1$ atm (1 bar), sometimes $T = 298$ K) and K_p is the equilibrium constant expressed in terms of partial pressure p. $\Delta G^o = $ -237,350 J mol^{-1} which can be converted in value into the standard emf $E^o = 1.23$ V. ΔG^o for the chemical reaction (24) has nothing to do with E^o, but it just represents $K_p = P_{H_2} P_{O_2}^{1/2} / a_{H_2O} = 10^{41.6} \gg 1$, suggesting that the degree of reaction advancement ξ exceeds 1/2.

Example 2. Let us then imagine the short-circuited state of the Daniell cell.

$$Zn + Cu^{2+,aq} = Zn^{2+,aq} + Cu \qquad (27)$$
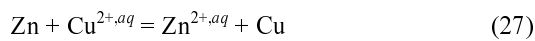
$$\Delta G^o = -RT \ln \frac{a_{Zn^{2+}}}{a_{Cu^{2+}}}$$

At 298 K, we calculated $\Delta G^o = $ -213,040 J mol^{-1} which can be converted in value into $E^o = 1.1$ V. ΔG^o for the reaction (27) is not physically related to the standard emf, which just represents historically an S. Glasstone's misconception, 1960[2]), but it merely represents $K_p = a_{Zn^{2+}}/a_{Cu^{2+}} = 1.98 \times 10^{37} \gg 1$. This means that Zn electrode has the same potential as Cu electrode.

Example 3. Finally, we come to equilibrium for the chemical reaction

$$C^s + O_2^g = CO_2^g \qquad (28)$$

$$\Delta G^o = -RT \ln \frac{P_{co_2}}{p_{o_2}}$$

At $T = 1173$ K = 900ºC, we calculated

$$\Delta G^o = \text{-395,085 J mol}^{-1}$$

$$K_p = \frac{p_{co_2}}{p_{o_2}} = 10^{17.59} \gg 1$$

As a result of mental experiment, Fig. 2 shows a schematic plot of Gibbs free energy G against degree of completion of the reaction ξ. From Fig. 2, it is readily seen that a large (-) ΔG^o gives a minimum on the right-hand side of Fig. 2 and leads to a very large equilibrium constant in terms of activity a, K_a. By contrast, a large (+) ΔG^o gives a minimum on the left-hand side and leads to a very small K_a. It should be noted that G value at both $\xi = 0$ and $\xi = 1$ is characterised with a distribution of δ–function.

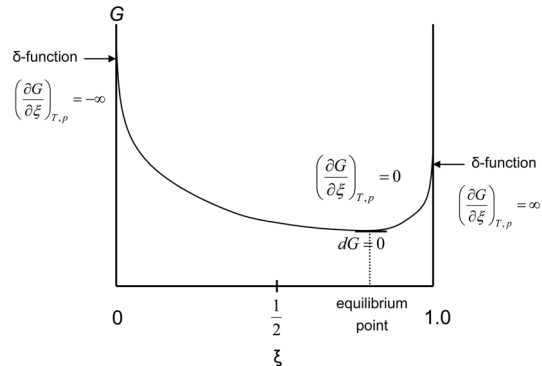As a result of mental experiment, Fig. 3 illustrates

Fig. 2. Gibbs free energy G as a function of degree of reaction advancement ξ (metal experiment).
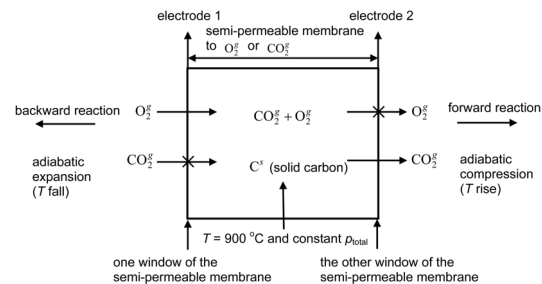

Fig. 3. Van't hoff equilibrium box model (mental experiment).

the device of the Van't Hoff equilibrium box. The carbon is thought to slowly burn away in the reaction box, which is equipped with two windows. One is permeable to oxygen only and the other to carbon dioxide only. Oxygen is slowly fed into the box through one window and carbon dioxide is slowly removed through the other window by means of a piston and cylinder. The equilibrium constant $K_p = p_{CO_2}/p_{O_2}$ is maintained at a value only infinitesimally less than the equilibrium value $10^{17.59}$. At the same time through the movement of the pistons, allowing for the processes of heating up and cooling down, the maximum useful work (ΔG) should be obtained.

However, we meet the two difficulties in the way of achieving such a process. One is seeking for the semi-permeable membrane for the purpose of with standing the pressure difference between the reactant (C + O$_2$) and the product (CO$_2$) $10^{17.59}$atm. The other is that the rate of permeation is always extraordinarily low.

We propose solution 1 to remove the first difficulty:

A big pressure difference can be transposed to a small potential difference by replacing the way of achieving a chemical equilibrium by the electrochemical way. We also propose solution 2 by means of an electrochemical cell to raise the permeation rate considerably and at the same time to achieve the thermodynamic efficiency greater than unity.

Solution 1. In the case of hydrogen permeation cell

cathodic side (') $2H^+ + 2e = H_2(100 \text{ atm})$

anodic side (") $H_2(1 \text{ atm}) = 2H^+ + 2e$

We calculated

$$E = \frac{RT}{2F}\ln\frac{p'_{H_2}}{p''_{H_2}} = \frac{8.134 \times 298}{2 \times 96500} \times 2.303\log\Delta P_{H_2}$$

$$= 0.03 \times 2 = 60\,\text{mV}$$

which is experimentally feasible.

Solution 2. The reaction $C^s + \frac{1}{2}O_2^g = CO^g$ should be used for production of electrical energy W_{ele} by means of the electrochemical cell. Since the entropy change ΔS is positive (+), it is easily expected that during the overall cell reaction not only ΔH is converted into W_{ele}, but also heat by $T\Delta S$ term can be additionally extracted from the surroundings which is converted along with ΔH into W_{ele}. Therefore, we calculated

η_{th} (thermodynamic efficiency of galvanic cell) $= \frac{\Delta G}{\Delta H} > 1$

5. Relationship between ΔG and E Including ΔG^o and E^o

There are two kinds of the Helmholtz's (E) and Nernst-Wargner's approaches ($E = \phi^c - \phi^a$) concerning emf in electrochemistry. As per the Helmholtz's approach, we write

$$dF = \delta W_{rev}(\text{max.}) = -pdV(\text{hydrostatic system}) \quad (29a)$$

On the analogy of dF, we find

$$dF = \delta W_{rev}(\text{max.useful}) = -EFdz \quad (29b)$$

which is consistent with the M. Planck's (IUPAC) sign convention ($dz > 0$).

The same result is obtained from the Helmholtz's approach as from the Nernst-Wagner's approach.

$$\Delta G = -zFE \quad (30a)$$

with $E^o = (\phi^c - \phi^a) > 0$

$$\Delta G^o = -zFE^o \quad (30b)$$

with $E^o = (\phi^{o,c} - \phi^{o,a}) > 0$

which is valid for IUPAC convention as well as American sign convention. For the readers' convenience, Table 2 shows similarity between hydrostatic and non-hydrostatic systems.

6. Electrochemical Equilibrium of Galvanic Cell Characterised by emf E, not by Equilibrium Constant in Terms of Activity a, K_a

Electrochemical equilibrium is uniquely characterised by emf E with a classic example, reversible Daniell cell (1836) (Volta cell).
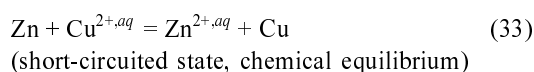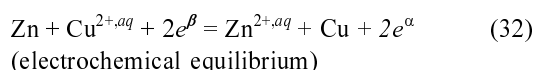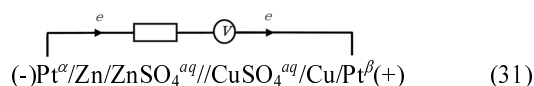
$$(-)Pt^\alpha/Zn/ZnSO_4^{aq}//CuSO_4^{aq}/Cu/Pt^\beta(+) \quad (31)$$

$$Zn + Cu^{2+,aq} + 2e^\beta = Zn^{2+,aq} + Cu + 2e^\alpha \quad (32)$$
(electrochemical equilibrium)

$$Zn + Cu^{2+,aq} = Zn^{2+,aq} + Cu \quad (33)$$
(short-circuited state, chemical equilibrium)

Table 2. Similarity of thermodynamic variables between hydrostatic (pdV) system and non-pdV system[5]

System	Intensive variables	Extensive variables	Work done
Hydrostatic system	P [bar] T [K]	V [m^3]	$-pdV$ [J]
Electrochemical cell	E [V] T [K]	z [C]	$-EFdz$ [J]
Surface energy	$-\gamma$ [N m^{-1}] T [K]	A [m^2]	$-\gamma dA$ [J]
Magnetic materials	$-\vec{B}_o$ [Weber m^{-2}]	M [A m^2]	$\vec{B}_o\,dM$ [J]
Dielectric materials	$-\vec{E}_o$ [V m^{-1}]	P [C m]	$\vec{E}_o\,dP$ [J]

Including electrical work δW_{ele} in pdV-work, the combined 1st and 2nd laws at constant T and p give

$$dU = \delta Q_{rev} + \delta W_{V,rev} + \delta W_{ele}$$
$$dU = TdS - pdV + \delta W_{ele}$$
$$\delta W_{ele} = dG = dU + pdV - TdS = dH - TdS$$
$$\text{where } \delta Q_{rev} = TdS$$

We write in other form

$$W_{ele} = \Delta G(z) = \Delta H(z) - T\Delta S(z)0$$

where $\delta Q_{rev} = TdS$, $\Delta G(z)$ means the isothermal and isobaric free energy (the maximum useful work, electrical energy) required (consumed, released) for (during) transfer (accumulation, detachment) of the electric charge z (ions or electrons). $\Delta H(z)$ and $\Delta S(z)$ mean the corresponding enthalpy and entropy, respectively.

If the irreversible (spontaneous) process occurs, we get

$$W_{ele} = \Delta H - Q \qquad (34)$$

where Q ranges between Q_{irr} and Q_{rev}. In view of Eqs. (22) and (34) we categorise W_{ele} into the following 3 cases:
For reversible change,

$$\left| W_{ele} \right| = \left| \delta G \right| = \left| W_{rev}(useful) \right|$$

For an irreversible (spontaneous) change,

$$\left| W_{ele} \right| < \left| \delta G \right| < \left| W_{rev}(useful) \right|$$

For the most eventual irreversible change,

$$\left| W_{ele} \right| = 0$$

which means the occurrence of the short-circuited corrosion.

Fig. 4 illustrates Daniell (equipped with membrane)/Volta cell (without membrane) with help of which it is feasible to completely convert the chemical energy into the electrical energy. Fig. 5 demonstrates local cell model how for corrosion process to proceed. The oxidising agent (oxidised species), e.g. O_2 in air depolarises the cell by reacting with H_2 formed to reduce hydrogen overvoltage, so that high corrosion current is produced during the cell operation. Such a depolarisation is sometimes desir-
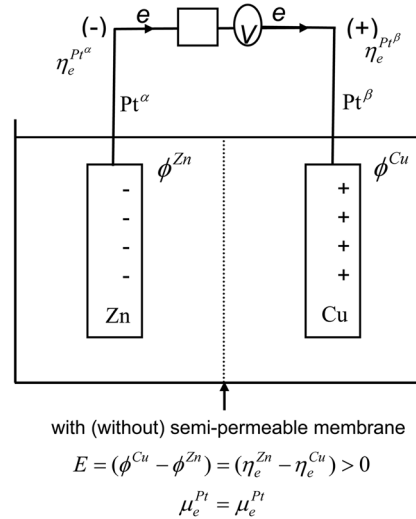

$$E = (\phi^{Cu} - \phi^{Zn}) = (\eta_e^{Zn} - \eta_e^{Cu}) > 0$$
$$\mu_e^{Pt} = \mu_e^{Pt}$$

Fig. 4. Scheme of a galvanic cell (Daniell cell/Volta cell).
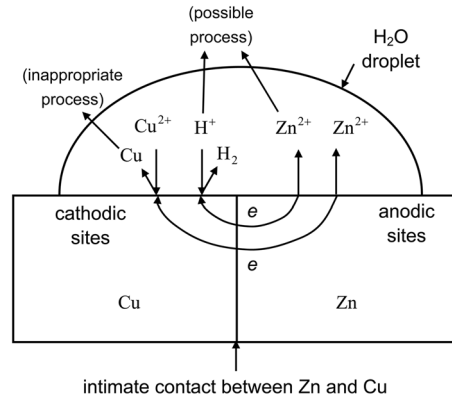

Fig. 5. Formation of local cell (corrosion, short-circuited state, depolarised state).

able or should be suppressed, depending upon the purpose of the cell.

We summarise $\Delta G(z)\{\Delta G^o(z)\}$ at constant T and p as the maximum useful work.

$$\Delta G(z) = -zFE(z)$$
(maximum useful work for the reversible process)
$$(35a)$$
$$\Delta G^o(z) = -zFE^o(z)$$
(maximum useful work for the reversible process at the standard state) $\qquad (35b)$

$\Delta G(\Delta G^o)$ has a fixed value for the reversible gal-

vanic cell as follows:

$$\Delta G = \Delta H - T\Delta S \qquad (36a)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad (36b)$$

From the condition of chemical equilibrium, we obtain the following expression

$$\Delta G^0 = - RT\ln k_a, \ K_a = \exp\left(-\frac{\Delta G^0}{RT}\right), \ \Delta G^0 = -zFE^0$$

It is noted that E^o ranges in value from 0 to a positive value and $K_a = exp(\Delta G^0/RT)$ ranges in value from 1 to a large (+) value. The equilibrium constant K_a is of no physical meaning for electrochemical equilibrium, but it is of significance only for chemical equilibrium, because the chemical potential gradient is always developed at electrochemical equilibrium.

For the Daniell cell (31) at $T = 298\,\text{K} = 15^o\text{C}$, thermodynamic data are given

$$\Delta G = \text{-211.3 kJ mol}^-1$$
$$\Delta H = \text{-235.2 kJ mol}^-1$$
$$T\Delta S = \text{-23.85 kJ mol}^-1$$

$$\Delta S = -\frac{23850}{288} = -82.8 \text{ J mol}^{-1}\text{ K}^{-1}$$

From the above equilibrium data, we recognise that ΔH (decrease) and ΔS (decrease) contribute not in collaborating way, but in conflicting way to ΔG (decrease in absolute value) in the Daniell cell, since the relation $\Delta G = \Delta H - T\Delta S$ should hold.
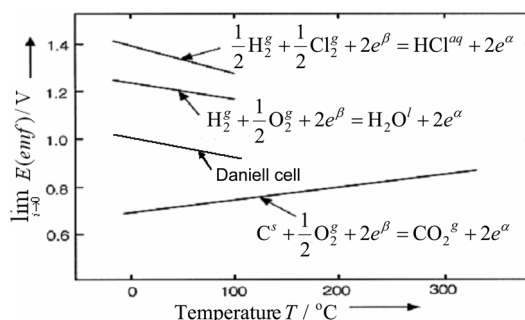

Fig. 6. Emf dependence on temperature for hydrogen-oxygen fuel cell, chlorine-hydrogen fuel cell and electro-chemical reaction $C^s + \frac{1}{2}O_2^g + 2e^\beta = CO^g + 2e^\alpha$.

Now we define thermodynamic (theoretical) efficiency of galvanic cell as

$$\eta_{th} = \frac{\Delta G(gain)}{\Delta H(pay)} = \frac{\Delta H - T\Delta S}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \qquad (37)$$

If $\Delta S < 0$, then $\eta_{th} < 1$, if $\Delta S > 0$, then $\eta_{th} > 1$. The latter η_{th} does not mean the thermodynamic efficiency in the sense, but it means the coefficient of performance of the galvanic cell. It is interesting to note that conversion of chemical energy for $C^s + \frac{1}{2}O_2^g = CO^g$ with the entropy increase into the electrical energy by means of the electrochemical cell. In this case, $\eta_{th} > 1$ is always valid.

Fig. 6 represents emf dependence on temperature from which we easily predict the thermodynamic efficiency of cell based upon $(\partial S/\partial z)_T = (\partial E/\partial T)_x$.

Table 3. Thermodynamic properties of H_2/O_2 fuel cell, Cl_2/H_2 fuel cell and O_2/CO_2 electrochemical equilibrium at 298 K

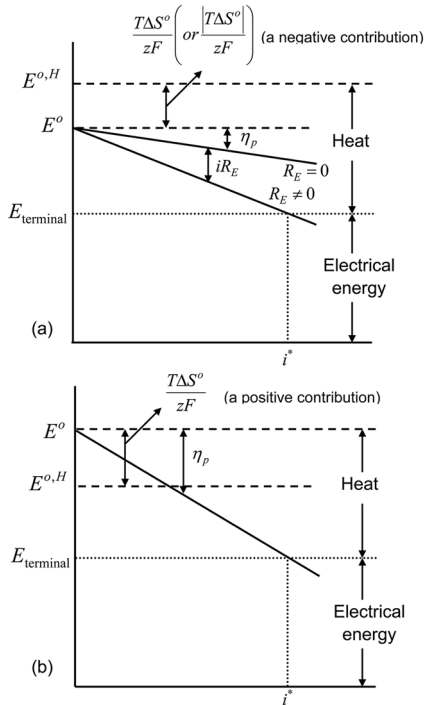|	$\left(\frac{\partial E^o}{\partial T}\right)_p = \left(\frac{\partial E^o}{\partial T}\right)_z = \frac{\Delta S^o}{zF}$ [mV K^{-1}]	$E^{o,H}$ [V]	E^o [V]	$\eta_{th} = \frac{E^o}{E^{o,H}}$ [-]
1. $H_2^g + \frac{1}{2}O_2^g + 2e^\beta = H_2O^l + 2e^\alpha$	-0.85	1.48	1.23	0.83
2. $H_2^g + \frac{1}{2}O_2^g + 2e^\beta = H_2O^g + 2e^\alpha$	-0.23	1.25	1.18	0.94
3. $Cl_s^g + H_2^g + 2e^\beta = 2HCl^g + 2e^\alpha$	-1.25 ~ -1.26	1.73	1.36	0.79
4. $CH_3OH^l + \frac{3}{2}O_2^g + 6e^\beta$ $= CO_2^g + H_2O^l + 6e^\alpha$		1.247	1.210	0.97
5. $C^s + \frac{1}{2}O_2^g + 2e^\beta = CO^g + 2e^\alpha$	0.46	0.57	0.71	1.25
6. $Zn^s + CuSO_4^g(\text{or } Cu^{2+}) + 2e^\beta$ $= Cu^s + ZnSO_4^g (\text{or } Zn^{2+}) + 2e^\alpha$	-0.453	1.218	1.094	0.90

Fig. 7. Schematic plots of potential against current density produced in the cell for the case (a) $\Delta S < 0$ and (b) $\Delta S > 0$ for the overall cell reaction where R_E = electrolyte resistance, hp = charge transfer overvoltage at two electrodes, ηres = iR_E = electrolyte resistance overvoltage, $E_{terminal}$ = terminal voltage and i^* = a specific current density produced.

Table 3 summarises the thermodynamic properties of different fuel cells from which we can easily sketch the plot of potential against current density produced in the cell. Fig. 7 illustrates the schematic diagram of potential vs. current density during the cell operation, depending upon the sign of the entropy portion of the overall cell reaction.

Now we come to the method how to measure the equilibrium electrode potential. We start with raising a question what we do understand by the reversible process of the galvanic cell. A specific quiz is to calculate internal (electrolyte) resistance R_i and terminal voltage V when emf E and external (wire) resistance R_a are given in Fig. 8(a). The clue to the quiz is found in Figs. 8(b) and 8(c).

IR drop through the electrolyte increases with increasing thickness. From Fig. 8(b), we get

If $R_i = 0,\quad E = E_c + |E_a|$

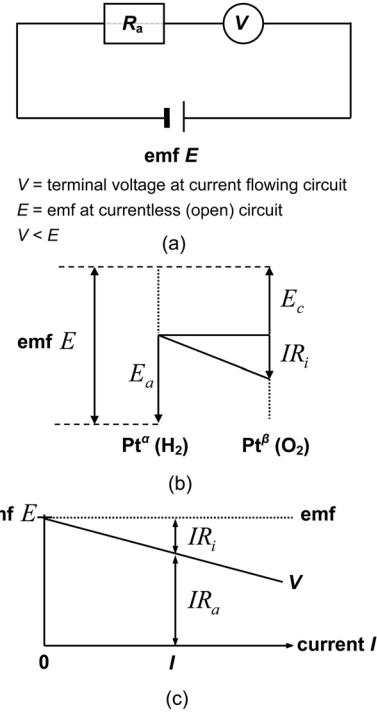Resistance polarisation (overvoltage) is given by

Fig. 8. (a) Relation between terminal voltage $E_{terminal}$ and emf E, (b) *IR* drop across the electrolyte and (c) cell voltage drop by discharging current I.

$$\eta_R = V - E \quad (\text{reference point} = IR_i)$$

From Fig. 8(c), we get

$$E = I(R_i + R_a) \quad (\text{Ohm's law}) \tag{38a}$$

$$V = IR_a \tag{38b}$$

Eliminating I from Eqs. (38a) and (38b), we get

$$V = E\left(\frac{R_a}{R_a + R_i}\right) \tag{39}$$

From Eq. (39), it is seen that as R_i goes down to a lower value and R_a rises up to a higher value, emf E approaches to V.

We differentiate between galvanic cell representing hill-down going automobile and electrolysis cell representing hill-up moving automobile. Fig. 9 illustrates the comparison of overvoltage between two cells. Emf is developed at $I = 0$. When anode and cathode are in short-circuit (point P), a zero voltage of cells is provided and maximum current I_P is delivered.
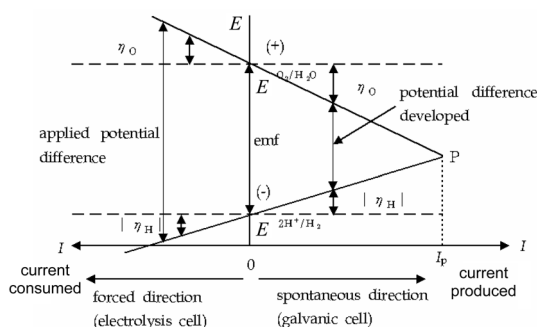
Fig. 9. Comparison of overvoltage (sign) between in galvanic cell and electrolysis cell.

Fig. 10(a) envisages the working principle of the Wheatstone's bridge. If no current flows between two branches through G, then the current flow is the same in the two branches as per the 1st Kirchhoff's law, $i.e.$ $I_s = I_x$ and $I_1 = I_2$. As per the 2nd Kirchhoff's law, $I_s \cdot R_s = I_1 \cdot R_1$ and $I_x \cdot R_x = I_2 \cdot R_2$ are valid.

$$\frac{R_x}{R_s} = \frac{R_2}{R_1} \qquad \therefore R_x = \frac{R_2}{R_1} R_s \qquad (40a)$$

From the above formula, two measuring methods are possible. One is to measure R_x by maintaining the ratio R_2/R_1 constant and varying R_s. The other is to measure R_x by maintaining R_s constant and varying the ratio.

From the Poggendorf's potentiometric circuit (Fig. 10(a)), it is seen that

$$\frac{E_x}{E_s} = \frac{AB'}{AB} \qquad \therefore E_x = \frac{AB'}{AB} E_s \qquad (40b)$$

We can determine unknown emf E_x from E_s by adjusting potential drops AB' and AB by zero current detector G.

In conclusion, the idea of equilibrium thermodynamics of the chemical reaction coupled with other interfacial (phase boundary) reactions can be readily extended to the idea of kinetics of mass transport (diffusion and migration) coupled (mixed) with other interfacial (charge transfer) reactions. In this case, the electrochemical reaction proceeds under the condition where mass transport through the electrode (or electrolyte) is kinetically mixed with charge transfer at the electrode/electrolyte interface, for example, cell impedance-controlled lithium intercalation into and deintercalation from transition metal oxide[11-20], mixed controlled hydrogen
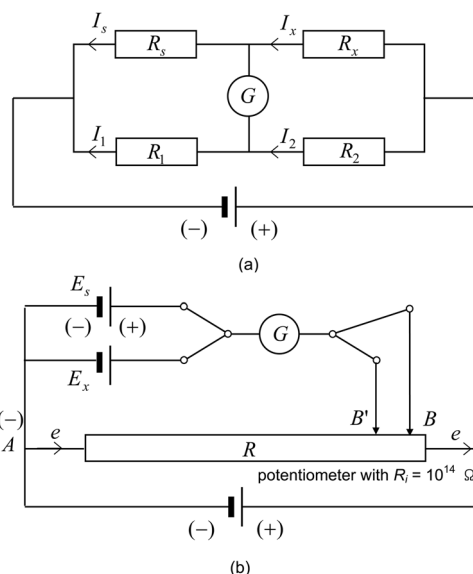

Fig. 10. (a) Principle of the Wheatstone's bridge and (b) the Poggendorf's potentiometric compensation method for determination of emf E_x. E_s = standard emf cell, "Weston-Cd-normal-cell", $T = 298$ K, $E_s = 1.018$ V. G = galvanometer (zero current detector).

transport through hydride forming electrode[21-27] and mixed controlled oxygen reduction at cathodes of PEMFC[28-30] and of SOFC[31-34].

7. Summary

1. (i) Gibbs free energy change ΔG before and after the chemical reaction originally defined as the maximum useful work is necessary at constant T and p to transfer particles (chemical species) between "internal" phases which is called "inner" chemical energy. (ii) ΔG acts as an arbiter between sometimes 2 collaborating factors of ΔH and ΔS to decrease during the irreversible (spontaneous) process and finally to become the minimum at reversible chemical equilibrium ("absence of any other constraints $e.g.$ electrical constraint" $\Delta G = 0$). (iii) Chemical equilibrium is uniquely characterised by the values of the equilibrium constant K_a (or ΔG^o).

2. (i) Modified (restrictive) Gibbs free energy change ΔG^+ before and after the electrochemical reaction is necessary at constant T and p to the transfer chemical potential (energy) superimposed on the electrical potential (energy). (ii) Electrochemical equilibrium is then established when the

decrease in chemical potential (energy) {consumption (-)} is compensated by the increase in useful electrical potential (energy) {gain (+)}. When the chemical energy with (-) value is coupled with other useful potential energy with (+) value, this charge transfer reaction between two phases is forced by that spontaneous chemical reaction. (iii) ΔG represents the maximum useful work at reversible electrochemical equilibrium of galvanic (electrolytic) cell ("presence of electrical constraint" $\Delta G \neq 0$).

Acknowledgements

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