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Thermodynamic theory of magnetic field effects on chemical equilibria and applications to metal–hydrogen systems

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Abstract

A general thermodynamic theory was constructed on magnetic field effects on chemical equilibria. Introducing the magnetochemical potential or the electromagnetic chemical potential leads to the magnetic field-induced changes in the equilibrium constant in an ideal gas reaction and the electromotive force in an electrochemical system. Applying these general results to metal–hydrogen systems gives the relationships between the equilibrium hydrogen pressure or the equilibrium electrode potential and magnetic fields, which correspond to experimental data.

Keywords: Magnetic field; Chemical equilibrium; Metal–hydrogen system; Equilibrium constant; Equilibrium electrode potential

1. Introduction

Scientists have long considered that magnetic fields do not markedly influence chemical systems because magnetic energies are much smaller than the energy which dominates chemical reactions, such as thermal, activation or binding energy. The magnetic energy, for instance, is about 12.5 mJ mole^{-1} in a magnetic field of 1 T for paramagnetic systems; in contrast, the thermal energy is 2.5 kJ mole^{-1} at room temperature. However, various effects of magnetic fields on chemical systems have been recently recognized in relation to kinetics or equilibria. The effects on reaction kinetics are typically shown by radical photochemical reactions under the influence of rather low magnetic fields [1,2] and the effects on reaction equilibria are clearly indicated by applying strong magnetic fields to metal–hydrogen systems [3,4]. For the $LaCo_5$–H system, the equilibrium hydrogen pressure, a measure of the chemical equilibrium, changes from 120 kPa in zero magnetic field to 180 kPa in 26 T [5]. Moreover, the equilibrium potential of a $LaCo_5H_x$ electrode in alkaline solution is shifted −1.64 mV due to an applied magnetic field of 15 T [6,7]. These results are the first observation showing that magnetic fields influence chemical equilibria. To explain the origin of these magnetic field effects, we have already obtained the formulae which relate the magnetic field with the equilibrium pressure or the equilibrium potential from the viewpoint of magnetic free energy [3,6].

In this paper, we focus our interest on the equilibrium aspect of the magnetic field effects. First a thermodynamic theory is systematically derived starting from the magnetic free energy in Section 2, where we introduce the magnetochemical potential or the electromagnetic chemical potential. Then, these general results are applied to metal–hydrogen systems in Section 3. As a result, we derive the formulae obtained previously and show the validity of the present theory.

2. Chemical equilibria in magnetic fields

2.1. Magnetochemical potential

For a chemical system under the influence of a magnetic field, we can define the thermodynamic potential G which is a natural function of temperature T, pressure P, the mole numbers N_i of the ith components ($i=1,2,...,k$) and the magnetic field strength $\boldsymbol{H}$. The complete differential of G is

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$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \sum_{i=1}^{k} \mu_i \mathrm{d}N_i - \int_{\bar{V}} \mathrm{d}\nu \mu_0 \boldsymbol{M} \mathrm{d}\boldsymbol{H} \tag{1}$$

where S is the entropy, μ_i is the chemical potential of the ith component, $\boldsymbol{M}$ is the magnetization, μ_0 is the permeability of a vacuum, $\mathrm{d}\nu$ is the element of volume and the integration extends over the volume of the system V. The last term in the right-hand side is the magnetic free energy from which the energy forming a magnetic field in a vacuum and the energy of the demagnetization field are eliminated.

The total magnetic moment of the system is considered to be additive for the molar magnetic moment $\boldsymbol{m}_i$ of the constituent components ($i=1,2,...,$k). Then, differentiating G with respect to the mole number N_i gives the chemical potential of the ith component as the sum of the non-magnetic and the magnetic terms, which is totally called as the magnetochemical potential:

$$\mu_i = \mu_i^{(0)} + \mu_i^{(m)} = \mu_i^{(0)} - \int_{H=0}^{H} \mu_0 \boldsymbol{m}_i \mathrm{d}\boldsymbol{H} \tag{2}$$

2.2. Equilibrium constant

We consider a reaction which occurs in a mixture of ideal gases under the influence of a magnetic field. The magnetochemical potential of the ith gas is

$$\mu_i = \mu_i^{(0)} + \mu_i^{(m)} = \mu_i^{*} + RT\,\ln(P_i/P^{*}) - \int_{H} \mu_0 \boldsymbol{m}_i \mathrm{d}\boldsymbol{H} \tag{3}$$

where μ_i^{*} is the chemical potential at the standard pressure P^{*} and a temperature T in zero magnetic field and P_i is the partial pressure of the ith gas. (Below we simply write P_i for P_i/P^{*}.)

A chemical equilibrium requires the condition that the change in the thermodynamic potential G must vanish for virtual changes in the mole numbers. This condition is generally expressed by

$$\sum_{i=1}^{k} \mu_i \nu_i = 0 \tag{4}$$

where ν_i denotes the stoichiometric coefficient for the ith component in the reaction. The sign of ν_i is taken to be negative for the reactants and positive for the products.

Applying the condition of chemical equilibrium to the ideal gas reaction gives the (pressure) equilibrium constant K_{P} as

$$-RT\,\ln K_{\mathrm{P}} = -RT\,\ln\left(\prod_{i=1}^{k} P_i^{\nu_i}\right) = \sum_{i=1}^{k} \nu_i \left(\mu_i^{*} - \int_{H} \mu_0 \boldsymbol{m}_i \mathrm{d}\boldsymbol{H}\right) \tag{5}$$

Comparing the equilibrium constant in zero magnetic field with that in a magnetic field, we have the following formula:

$$\frac{K_{\mathrm{P}}^{[H]}}{K_{\mathrm{P}}^{[0]}} = \exp\left(\frac{1}{RT}\sum_{i=1}^{k} \nu_i \int_{H=0}^{H} \mu_0 \boldsymbol{m}_i \mathrm{d}\boldsymbol{H}\right) \tag{6}$$

where the superscripts [0] and [H] mean the quantities in zero magnetic field and the magnetic field, respectively.

2.3. Electromotive force

Let us suppose a half electrochemical cell which is composed of two phases. The α phase including the ions ($i=1,...,j$) is at the electric potential of ψ_{α} and the β phase including the ions ($i=j+1,...,k$) is at the electric potential of ψ_{β}. Under the influence of a magnetic field of H, the chemical potential of the ith ion is considered to consist of the non-electromagnetic, the electric and the magnetic terms:

$$\begin{aligned} \mu_i &= \mu_i^{(0)} + \mu_i^{(\mathrm{e})} + \mu_i^{(\mathrm{m})} \\ &= \mu_i^{*} + RT\,\ln(x_i/x^{*}) + z_i F \psi_{\alpha} - \int_{H} \mathrm{d}\nu \mu_0 \boldsymbol{m}_i \mathrm{d}\boldsymbol{H} \end{aligned} \tag{7}$$

where z_i is the valence of the ith ion and F is the Faraday constant. x_i is the concentration of the ith ion and x^{*} is the standard concentration at a temperature of T in zero magnetic field. (Below we use the convention $x_i/x^{*} \rightarrow x_i$.)

Because the α phase is chemically equilibrated with the β phase, the electromotive force between the two phases is derived using Eq. (4):

$$\epsilon = \psi_{\alpha} - \psi_{\beta} = \frac{1}{Fn}\sum_{i=1}^{k} \nu_i \left(\mu_i^{*} + RT\,\ln x_i - \int_{H} \mu_0 \boldsymbol{m}_i \mathrm{d}\boldsymbol{H}\right) \tag{8}$$

where n is the total charge transfer by the reaction.

$$n = -\sum_{\substack{i=1 \\ (\alpha-\mathrm{phase})}}^{j} \nu_i z_i = \sum_{\substack{i=j+1 \\ (\beta-\mathrm{phase})}}^{k} \nu_i z_i \tag{9}$$

Finally, the electromotive force of the half cell is shifted by magnetic fields as

$$\Delta\epsilon = \epsilon^{[H]} - \epsilon^{[0]} = \frac{-1}{Fn}\sum_{i=1}^{k} \nu_i \int_{H=0}^{H} \mu_0 \boldsymbol{m}_i \mathrm{d}\boldsymbol{H} \tag{10}$$

2.4. Phase rule of chemical reactions in magnetic fields

Let us suppose the chemical system which is composed of c reactions, k components and m phases under the influence of a magnetic field. For the system, the numbers of intensive parameters is $k+3$ because of T, P, $\boldsymbol{H}$, μ_1, μ_2,...,μ_k. Between these parameters the Gibbs–Duhem relation holds in each phase and the equilibrium condition holds for each reaction. Therefore, the number of independent parameters, that is the degree of freedom, is

$$f = k + 3 - m - c \tag{11}$$

3. Metal hydrogen systems

3.1. Gas solid reaction

In a so-called plateau region, two hydrides MH_a and MH_b coexist with hydrogen gas according to

$$\left(\frac{2}{b-a}\right)MH_a + H_2 = \left(\frac{2}{b-a}\right)MH_b \tag{12}$$

where M stands for a metal or intermetallic compound, e.g., M=$LaCo_5$. First, we test the phase rule in a magnetic field. There is one reaction ($c=1$), three components ($k=3$) and three phases ($m=3$) in this system. Thus, the phase rule of Eq. (11) gives the degree of freedom $f=2$. This means that the plateau pressure still appears as long as the system is influenced by a constant magnetic field at a constant temperature. In fact, the β–γ region for the $LaCo_5$–H system showed the plateau pressure in a constant magnetic field of 12 T [8].

In this reaction the pressure equilibrium constant depends on only the hydrogen pressure P_{H2}. That is, $K_P = P_{H_2}^{-1}$. The two hydrides have the molar magnetic moment of m_a and m_b and hydrogen has no magnetic moment. Consequently, Eq. (6) yields the logarithmic pressure change (LPC)

$$\ln(P_{H_2}^{[H]}/P_{H_2}^{[0]}) = \frac{2}{RT}\int_{B_0=0}^{B_0} \Delta M \mathrm{d}B_0 \tag{13}$$

where B_0 is the applied magnetic filed expressed in the units of T, that is, $B_0=\mu_0 H$. ΔM is the change in magnetic moment of the hydride MH_x per desorbed mole hydrogen, which is defined to be positive when the moment is increased upon desorption of hydrogen.

$$\Delta M = \frac{m_a - m_b}{b-a} \tag{14}$$

In general the molar magnetic moment m_a or m_b depends on H. However, if the two hydrides are ferromagnetic, the magnetic moment is saturated to the saturation moment of $m_a^{(s)}$ and $m_b^{(s)}$ in very low magnetic fields. Eq. (14) is written in this case:

$$\ln(P_{H_2}^{[H]}/P_{H_2}^{[0]}) = \frac{2B_0\Delta M_s}{RT} \tag{15}$$

where ΔM_s [JT^{-1} (mole H)$^{-1}$] is the change in saturation moment of the hydrides per desorbed mole H. This relation has already been deduced from a thermodynamic consideration in previous work [3].

The molar magnetic moment m_i [JT^{-1} mole^{-1}] for a paramagnetic or diamagnetic hydride is proportional to H [Am^{-1}]. We define the molar susceptibility $\chi_i^{(m)}$ of the ith component as

$$m_i = \chi_i^{(m)}\mu_0 H = \chi_i^{(m)} B_0 \tag{16}$$

where $\chi_i^{(m)}$ is expressed in the unit of [JT^{-2} mole^{-1}]. In this case:

$$\ln(P_{H_2}^{[H]}/P_{H_2}^{[0]}) = \frac{B_0^2\Delta\chi}{RT} \tag{17}$$

where $\Delta\chi$ [JT^{-2} (mole H)$^{-1}$] means the change in susceptibility of the hydrides per desorbed mole H:

$$\Delta\chi = \frac{\chi_a^{(m)} - \chi_b^{(m)}}{b-a} \tag{18}$$

3.2. Metal hydride electrode

A metal hydride reacts in alkaline solution and constructs a half electrochemical cell:

$$\frac{1}{b-a}MH_a + H_2O + e^- = \frac{1}{b-a}MH_b + OH^- \tag{19}$$

Then, we estimate the magnetic field-induced shift in electromotive force according to Eq. (10) where $n=-1$ by Eq. (9).

$$\Delta\epsilon = -\frac{1}{F}\int_{B_0=0}^{B_0} \Delta M \mathrm{d}B_0 \tag{20}$$

In particular, this equation is converted to the following forms for a saturated ferromagnetic and a paramagnetic system, respectively:

$$\Delta\epsilon = -\frac{B_0\Delta M_s}{F} \tag{21}$$

$$\Delta\epsilon = -\frac{B_0^2\Delta\chi}{2F} \tag{22}$$

We have already obtained the formula of Eq. (21) by balancing the magnetic free energy with the electrochemical potential in previous work [6]. For a metal hydride electrode in acid solution, we have exactly the same relations as Eqs. (20)–(22).

3.3. Comparison with experiments

3.3.1. Paramagnetic hydride

We consider the Pd–H system as an example of the paramagnetic hydride. The equilibrium hydrogen pressure is $P_{H2}^{[0]} = 4\times10^4$ Pa in the α–β region at 393 K. The α phase $PdH_{0.03}$ is paramagnetic with the molar susceptibility of $\chi_\alpha^{(m)} = 4\times10^{-3}$ JT^{-2} mole^{-1} at 393 K [9]. On the other hand, the β phase $PdH_{0.6}$ loses the paramagnetism with $\chi_\beta^{(m)}=0$. Then, the change in susceptibility per desorbed mole hydrogen defined by Eq. (18) is $\Delta\chi = 7\times10^{-3}$ JT^{-2} (mole H)$^{-1}$.

Thus, the LPC, according to Eq. (17), is estimated to be $\mathrm{LPC}=2\times10^{-4}$ for $B_0=10$ T and $\mathrm{LPC}=1.8\times10^{-3}$ for $B_0=30$ T. These values approximately correspond to the pressure increase of 0.02% and 0.18%. We need a very sophisticated experiment to observe these pressure changes.

We, moreover, simulate the change in equilibrium potential for a PdH_x electrode using Eq. (22). Then, $\Delta\epsilon=-3.6$ and -32 μV by applied fields of $B_0=10$ and 30 T, respectively. These may be detectable if electric measurement for the potential is not disturbed by electromagnetic noise.

3.3.2. Ferromagnetic hydride

The magnetic field effects on the equilibrium pressure and the electromotive force have already observed for ferromagnetic hydride–hydrogen systems [3–7]. Obviously, the ferromagnetism of the hydrides causes the magnetic free energy to be so large to exhibit those magnetic effects clearly.

In the β–γ region for the LaCo_5–H system, the magnetic moment of the hydrides is decreased with increasing hydrogen composition by $\Delta M_s=16.4\ \mathrm{JT}^{-1}\ (\mathrm{mole\ H})^{-1}$ at room temperature [3]. According to Eq. (15), we expect that the hydrogen pressure is linearly increased with magnetic field. The experimental result in Ref. [3] showed such a linear increase in the pressure up to $B_0=14$ T. Moreover, the calculated value of $\mathrm{LPC}=0.189$ for $B_0=14$ T satisfactorily agreed with the observed value of $\mathrm{LPC}=0.192$. In the experiment in higher magnetic fields up to 26 T [5], the LPC tended to deviate from the linear curve in magnetic fields above 15 T. However, this tendency was explained by taking account of the magnetic field dependence of ΔM according to Eq. (13) [5].

The electromotive force of a $\mathrm{LaCo}_5\mathrm{H}_x$ electrodes was measured in magnetic fields up to 15 T [6]. The electrode hydride had a composition in the α–β region with the magnetic property of $\Delta M_s=8.7\ \mathrm{JT}^{-1}\ (\mathrm{mole\ H})^{-1}$. Therefore, we expect the magnetic field-induced change in electromotive force $\Delta\epsilon=-13.5$ mV for $B_0=15$ T according to Eq. (21). This value agreed well with the observed one $\Delta\epsilon=-1.64$ mV, accompanied with the proportionality of $\Delta\epsilon$ against magnetic field B_0, which was implied in Eq. (21) also.

As described above, the experimental results were completely explained by the formulae derived. In conclusion, the magnetic field effects on chemical equilibria can be generally understood by the thermodynamic scheme developed in this paper.

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