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ORIGINAL ARTICLE

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Extension of Gibbs–Duhem equation including influences of external fields

Abstract Gibbs–Duhem equation is one of the fundamental equations in thermodynamics, which describes the relation among changes in temperature, pressure and chemical potential. Thermodynamic system can be affected by external field, and this effect should be revealed by thermodynamic equations. Based on energy postulate and the first law of thermodynamics, the differential equation of internal energy is extended to include the properties of external fields. Then, with homogeneous function theorem and a redefinition of Gibbs energy, a generalized Gibbs–Duhem equation with influences of external fields is derived. As a demonstration of the application of this generalized equation, the influences of temperature and external electric field on surface tension, surface adsorption controlled by external electric field, and the derivation of a generalized chemical potential expression are discussed, which show that the extended Gibbs–Duhem equation developed in this paper is capable to capture the influences of external fields on a thermodynamic system.

Keywords Energy postulate · Electric field · Surface tension · Adsorption · Chemical potential

1 Introduction

The Gibbs–Duhem equation describes the relation among changes in temperature, pressure and chemical potential for components in a thermodynamic system [1–3]. This equation is named after Josiah Willard Gibbs and Pierre Duhem, Gibbs first obtained [4] and then Duhem gave the earliest critical examination and a general proof of it [5]. Gibbs–Duhem equation is regarded as one of the fundamental equations in thermodynamics, together with the differential equations of internal energy, enthalpy, free energy, and Gibbs function [1–3]. It plays an important role in Gibbs' definition of the ideal gas mixture as well as in his treatment of the phase rule [6]. It shows that in a thermodynamic system all the intensive properties are not independent but related, which makes it a mathematical statement of the state postulate. This equation is a criterion for thermodynamic consistency and finds some applications in phase equilibrium and chemical equilibrium; for example, a thermodynamic consistency test for vapor–liquid equilibrium data can be based on the Gibbs–Duhem equation, which is a powerful check on the apparent accuracy of the experimental data [7]. It is also helpful in calculating partial molar quantity of a binary mixture by measuring the composition of the mixture which depends on the total molar quantity, for example, the activity coefficients and the partial vapor pressures [8].

Enhancement of transfer processes with external fields, such as heat transfer or mass transfer enhancement with external electric field, is an effectively novel method [9]. Also, a thermodynamic system can be controlled

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by external fields [10]. Thus, it is desirable to understand these phenomena in the view point of thermodynamics, and so it is necessary to include the properties of external fields in the thermodynamic relations. Based on the energy postulate, a generalized Gibbs–Duhem equation with influences of external fields is derived in this paper. Then some applications of this generalized equation are shown as demonstrations, including the influences of external fields on surface tension and surface adsorption, and the derivation of a generalized chemical potential expression.

2 Extension of Gibbs–Duhem Equation with influences of external fields

The traditional Gibbs–Duhem equation is [1–3]

$$S\mathrm{d}T - V\mathrm{d}p + \sum n_i \mathrm{d}\mu_i = 0 \tag{1}$$

where S and T are entropy and absolute temperature, V volume, p pressure, n_i and μ_i are the number of moles and the chemical potential of component i, respectively. This equation shows that the pressure, temperature and chemical potentials of a system cannot change independently; especially the chemical potentials of a mixture cannot change independently. For example, for a two-component system during a constant temperature and constant pressure process, the equation leads to $n_1\mathrm{d}\mu_1 + n_2\mathrm{d}\mu_2 = 0$, which means that $\mathrm{d}\mu_1$ and $\mathrm{d}\mu_2$ must be in opposite sign, and that a small $\mathrm{d}\mu_1$ could lead to a large $\mathrm{d}\mu_2$ if n_1/n_2 is large. This equation is valid for a multiphase/multicomponent system [11], and also for all partial molar properties of a mixture [1–3].

The physical meaning of the first law of thermodynamics, $\mathrm{d}U = \delta Q + \delta W'$, is that the increase in internal energy $\mathrm{d}U$ is equal to the sum of the heat δQ absorbed by the system and the work $\delta W'$ done on the system. For a multicomponent system, or an open system which has material exchange with outside, if there are only heat transfer and the volume work with the outside, the fundamental thermodynamic equation for the system is [1] $\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum \mu_i \mathrm{d}n_i$. This differential equation also reveals that the internal energy of the system is the function of entropy, volume, and amount of substance of the system, that is $U = U(S, V, n_i)$.

According to energy postulate [12,13], the differential expression of any form of energy can be expressed as a product of a basic intensive property (X) and a differential of the corresponding basic extensive property (Y), $\mathrm{d}W = X\mathrm{d}Y$, in which the intensive property (X) represents a kind of field quantity. For example, gravitational potential energy is the product of gravitational constant (g), height (h) and mass (m), $gh\mathrm{d}m$; surface energy is the product of surface tension (γ) and surface area (A), $\gamma \mathrm{d}A$; electric energy is the product of electric potential (ϕ) and the amount of electric charge (q), $\phi \mathrm{d}q$; while the polarized energy is the product of electric field (E) and the total dipole moment (P'), $E\mathrm{d}P'$, etc. Because the change of energy, or the transferred energy, is equal to work/heat, so the differential expression $X\mathrm{d}Y$ can also be interpreted as a kind of work. Therefore, in addition to heat transfer, volume work, and material exchange, when there are j kinds of external fields acting on a system, according to the first law of thermodynamics and the energy postulate, the fundamental thermodynamic equation of the system can be extended to [13]

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum \mu_i \mathrm{d}n_i + \sum X_j \mathrm{d}Y_j \tag{2}$$

The classical definition of Gibbs energy is $G = U - TS + pV$, which can be interpreted that Gibbs energy is equal to the Helmholtz energy ($U - TS$) minus volume work ($-pV$). So in the presence of external fields, this definition can be extended to $G_\mathrm{f} = U - TS + pV - \sum X_j Y_j$. For example, in order to apply thermodynamics to dielectrics in the presence of electric fields, Guggenheim [3] redefined the Gibbs energy as $G_\mathrm{f} = U - TS + pV - EP'$; while in the thermodynamic study of interfacial system [14], the Gibbs energy is defined as $G_\mathrm{f} = U - TS - \gamma A$, where the volume term disappears because of the Gibbs dividing surface convention. Substituting the differential internal energy, now the differential Gibbs energy is

$$\mathrm{d}G_\mathrm{f} = -S\mathrm{d}T + V\mathrm{d}p + \sum \mu_i \mathrm{d}n_i - \sum Y_j \mathrm{d}X_j \tag{3}$$

This differential expression shows that the redefined Gibbs energy is a function of the quantities $T, p, \ldots, n_i, \ldots, X_j, \ldots$, that is $G_\mathrm{f} = G(T, p, \ldots, n_i, \ldots, X_j, \ldots)$.

If for an arbitrary positive number λ, a function $f(x_1, \ldots, x_i, \ldots)$ is hold for the relation $f(\lambda x_1, \ldots, \lambda x_i, \ldots)$ $= \lambda^k f(x_1, \ldots, x_i, \ldots)$, it is said to be homogeneous of degree k in the variables $x_1, \ldots, x_i, \ldots$. Differentiating both sides of this definition equation with respect to λ and then choosing $\lambda = 1$ leads to

$$\sum x_i \left(\frac{\partial f}{\partial x_i} \right) = kf \tag{4}$$

which is Euler's homogeneous function theorem [15]. Thermodynamic variables are either extensive whose magnitude is additive for subsystems or intensive whose magnitude is independent of the extent of the system. Intensive functions are homogeneous of degree zero, while extensive functions are homogeneous of degree one. If the amount of substance of a system increases λ times while keeping all the intensive variables constants, all the extensive, including the Gibbs energy, would also increase λ times, that is

$$G_f(T, p, \ldots, X_j, \ldots, \lambda n_1, \ldots, \lambda n_i, \ldots) = \lambda G_f(T, p, \ldots, X_j, \ldots, n_1, \ldots, n_i, \ldots) \tag{5}$$

Equation (5) means that the redefined Gibbs energy is homogeneous function of degree one, $k = 1$, in the variables of the amount of substance. So from Eq. (4), one can get

$$G_f = \sum n_i \left(\frac{\partial G_f}{\partial n_i} \right)_{T, p, X_j, n_{k \neq i}} \equiv \sum n_i \mu_i \tag{6}$$

where the definition of chemical potential $\mu_i = (\partial G_f / \partial n_i)_{T, p, X_j, n_{k \neq i}}$ is employed. Equation (6) is mathematically identical equation, because only one mathematical condition is used during the derivation, which is that the extended Gibbs energy is a function of intensive properties and the amount of substance [1, 2]. Thus, it can be differentiated as usual

$$dG_f = \sum n_i d\mu_i + \sum \mu_i dn_i \tag{7}$$

Substituting Eq. (7) into Eq. (3) leads to

$$S dT - V dp + \sum n_i d\mu_i + \sum Y_j dX_j = 0 \tag{8}$$

This is the desired generalized Gibbs–Duhem equation with influences of external fields. The last term represents the influences of external fields. This equation shows that all the intensive properties of a system, including the applied external fields, are related by this differential equation. If there is no external field, it returns to the classical Gibbs–Duhem equation.

3 Some applications of the extended Gibbs–Duhem equation

3.1 The influences of temperature and electric field on surface tension

The interface causes an increasing interest because a better understanding of natural processes and many technological applications are associated with it. In the presence of two phases, the interface is located in between them, which is not an infinitesimal sharp boundary in the direction of its normal, but it has a certain thickness. In the ideal Gibbs model [16], the whole system is divided into three parts, two are the bulk phases, and one is the interface which has negligible thickness and thus no volume. Thermodynamic relations can be applied to these three parts individually. The most important property of interface is surface tension, which describes how difficult it is to extend the area of a surface. The mechanical energy needed to increase a surface is $dW^\sigma = \gamma dA$ [16]. Applying the generalized equation (8) to the surface phase results in

$$S^\sigma dT + \sum n_i^\sigma d\mu_i + A d\gamma = 0 \tag{9}$$

The superscript σ indicates that these properties belong to the surface system. Equation (9) can be rewritten to

$$d\gamma = -\frac{S^\sigma}{A} dT - \sum \frac{n_i^\sigma}{A} d\mu_i \tag{10}$$

This equation reveals the dependence of surface tension on temperature and composition. For example, Eq. (10) implies that $s = -(\partial \gamma / \partial T)$, where $s = S^\sigma / A$ is the entropy per unit surface area, or superficial entropy. Because entropy is positive, this partial equation says that the surface tension decreases with temperature, which is obviously in accordance with empirical evidences. If the superficial entropy is approximated to be independent on temperature, integration of this partial equation leads to
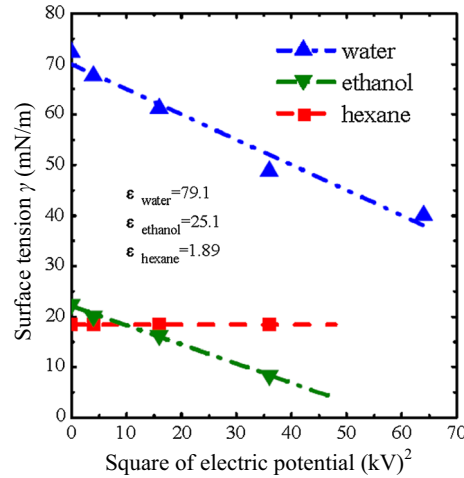
$$\gamma = \gamma_1 - s(T - T_1) \tag{11}$$

Fig. 1 Variations of surface tensions of water, ethanol, and hexane with square of applying voltage. The data are taken from Figs. 4 and 5 of Ref. [18] at 2 ms of elapsed time

This equation has the same form with the empirical expression $\gamma \approx \gamma_0(1 - T/T_c)$ if the integration constants were redefined [1]. For example, if the constants in Eq. (11) were chosen as $\gamma_1 \approx \gamma_0(1 - T_1/T_c)$, $s = \gamma_0/T_c$, then these two equations are identical.

Dielectric substances can be polarized in an electric field, which are associated with polarization energy. The differential expression of polarization energy is [17] $dW_p = E \cdot dP'$, and it can be simplified to $E\,dP'$ for an isotropic substance, $P' = PV$, P is the dipole moment of substance per unit volume (often called as polarization). The polarization is proportional to external electric field [17], $P_i = \varepsilon_0(\varepsilon_i - 1)E$, where ε_i is relative permittivity. For an ideal multicomponent mixture, the total electric dipole moment can be expressed as $P' = \sum n_i V_{m,i} P_i$, where $V_{m,i}$ is molar volume.

Thus, if there is an external electric field acting on the surface system, applying Eq. (8) to it and with small arrangement result in

$$d\gamma = -\frac{S^\sigma}{A}dT - \sum \frac{n_i^\sigma}{A}d\mu_i - \frac{P'^\sigma}{A}dE \tag{12}$$

This equation reveals the dependence of surface tension on temperature, composition and external electric field. For example, it gives the partial relation $P = -(\partial\gamma/\partial E)_T$, where $P = P'^\sigma/A$ is surface polarization. For one-component system, the surface polarization can be expressed as $P = \Gamma V_m \varepsilon_0(\varepsilon - 1)E$, here $\Gamma = n^\sigma/A$ is referred to surface excess [16]. Hence, at constant temperature, the surface tension can be integrated to

$$\gamma = \gamma_0 - \frac{1}{2}\Gamma V_m \varepsilon_0(\varepsilon - 1)E^2 \tag{13}$$

This equation says that the surface tension linearly decreases with the square of external electric field. Lippmann [16] derived an expression of the surface tension at a metal-electrolyte interface as a function of applied potential, $\gamma = \gamma_0 - (1/2)C^A U^2$, where C^A is surface capacitance, and also proved it with the measurement of mercury surface tension. If the relation between electric potential and electric field, $U = Ed$, is taken into account, Lippmann's relation is similar to Eq. (13).

Sato et al. [18] carried out an experimental study on the change in the surface tension of a liquid by applied voltage, part of their findings are transformed and plotted in Fig. 1. This figure reveals several features which can be explained with Eq. (13). (a) The surface tension decreases with applied field, and the reduction of surface tension due to the applied voltage is linearly proportional to the square of the voltage, hence the electric field for a fixed separation of the electrodes. (b) The variation of surface tension for distilled water is obvious, that for ethanol is smaller but noticeable, while the applied voltage had no observable effect for hexane. The reason is that, Eq. (13) shows that the reduction of surface tension is proportional to permittivity, and the permittivity of water is the largest, that of hexane is the smallest. (c) Sato also mentioned that changing the applied voltage polarity had no effect. The reason is as this, Eq. (13) shows that the reduction is proportional to the square of the electric field, which means that it only depends on the magnitude of the electric field and has no relation with its direction.

To numerically estimate the decrease in surface tension with external electric field, we need to know the surface excess. For a rough estimation, the liquid can be pictured as being arranged in a cubic structure, the volume of one unit cell is V_m/N_A, the dimension of the cell is $(V_m/N_A)^{1/3}$. Then the amount of substance per unit area in one layer is $N_A^{-1/3}V_m^{-2/3}$. If the surface is assumed to consist of k layers, then the surface excess is $\Gamma = kN_A^{-1/3}V_m^{-2/3}$. So the decrease in the surface tension for a pure substance due to external electric field can be expressed as $\gamma = \gamma_0 - (k/2)(V_m/N_A)^{1/3}\varepsilon_0(\varepsilon - 1)E^2$. Numerical estimation with this relation shows that the order of magnitude of the applied electric field should be at least 10^8 V/m for a noticeable decrease in the surface tension, which agrees with Kamienski's conclusion [19]. However, the electric charge existing on the liquid surface can produce strong local field, the actual applied field could be much smaller than this value [18].

3.2 Surface adsorption controlled by external electric field

Adsorption is the adhesion of small particles (molecules) from a gas or liquid to a surface. It is present in many natural, physical, biological, and chemical systems, and is widely used in industrial applications (activated carbon) such as mixture separation, air cleaning, water purification and adsorption chiller. Adsorption of proteins is of great importance when a material is in contact with blood or body fluids. Adsorption is a surface phenomenon, which is a consequence of surface energy. The present popular thermodynamic theory of adsorption is Gibbs adsorption equation [16,20], which is an equation used to relate the changes in concentration of a component in contact with a surface with changes in the surface tension. From Eq. (10), one can get $d\gamma = -\sum \Gamma_i d\mu_i$ at constant temperature, where $\Gamma_i = n_i/A$ is surface excess, this equation is called Gibbs adsorption equation (isotherms), it is the fundamental equation to capture the phenomena of adsorption. The simplest application of the Gibbs adsorption equation is a system of two components, e.g., a solvent 1 and a solute 2. For this binary system, the Gibbs adsorption equation is $-d\gamma = \Gamma_1 d\mu_1 + \Gamma_2 d\mu_2$. Moreover, since the surface excess quantities are defined relative to an arbitrarily chosen dividing surface, it is possible in principle to place that surface such that $\Gamma_1 = 0$. With the expression of chemical potential of an ideal solute $\mu_2 = \mu_2^0 + RT \ln(c_2/c_0)$, here c is the concentration of the solute, the traditional Gibbs adsorption equation can be expressed as [16,20]

$$\Gamma_2^1 = -\left(\frac{1}{RT}\frac{d\gamma}{d\ln c_2}\right) \tag{14}$$

The superscript "1" reminds of the special choice of the interface, that is $\Gamma_1 = 0$. This equation means that when the solute can decrease the surface tension, $d\gamma/dc_2 < 0$, thus the surface energy, then the solute is enriched in the interface, and there is an actual surface excess of solute. On the other hand, if the surface tension increases upon addition of solute, $d\gamma/dc_2 > 0$, the surface excess is negative, then the solute is depleted in the interface and there is a surface deficiency of solute.

Experiments show that surface adsorption can be enhanced by external electric field [21,22]. The thermodynamic mechanism of this enhancement can be captured by the extended Gibbs–Duhem equation developed in this paper. Applying Eq. (8) to surface phase acted by external electric field leads to

$$S^\sigma dT + \sum n_i^\sigma d\mu_i + A d\gamma + P'^\sigma dE = 0 \tag{15}$$

With the definitions of total electric dipole moment and the polarization mentioned above, the last term can be expressed as $P'^\sigma dE = \sum n_i^\sigma \left[\frac{1}{2}\varepsilon_0(\varepsilon_i - 1)V_{m,i}\right]dE^2$. Substituting this expression, dividing both sides by the surface area A, and at constant temperature, Eq. (15) can be simplified to

$$d\gamma = -\sum \Gamma_i \left[d\mu_i + \frac{1}{2}\varepsilon_0(\varepsilon_i - 1)V_{m,i}dE^2\right] \tag{16}$$

This is the extended Gibbs adsorption equation. The properties of external electric field are included in this equation, which represents the influence of the external electric field on the adsorption. For a two-component system, and with an appropriate dividing surface, the surface excess can be found from Eq. (16)

$$\Gamma_2^1 = -\left[\left(\frac{1}{RT}\frac{d\gamma}{d\ln c_2}\right)^{-1} + \left(\frac{1}{\frac{1}{2}\varepsilon_0(\varepsilon_2 - 1)V_{m,2}}\frac{d\gamma}{dE^2}\right)^{-1}\right]^{-1} \tag{17}$$

The last term in the bracket represents the contribution to the adsorption from external electric field; and if there is no external field, this term disappears, then Eq. (17) returns to the original Eq. (14). If an external electric field is present, this new equation directly tells us that when the surface tension decreases with electric field, $d\gamma/dE^2 < 0$, thus the surface energy decreases with electric field, then exertion of external electric field can increase the surface excess. Equation (13) shows that the surface tension decreases with electric field, thus, electric field can increase the adsorption, which was proved by experiments [21,22].

3.3 Chemical potential with the influences of external fields

Chemical potential is not only the criterion to estimate chemical equilibrium but also the causes of diffusions, phase transitions and chemical reactions [1–3]. The thermodynamic systems or processes acted by external fields can also be described by chemical potentials with the influences of external fields. The extensive thermodynamic quantity Y_j is proportional to the amount of substance, that is $Y_j = \sum n_i \left(\partial Y_j / \partial n_i \right)$, where $\partial Y_j / \partial n_i$ is partial molar quantity, then the generalized expression (8) can be rewritten as

$$S\mathrm{d}T - V\mathrm{d}p + \sum_i n_i \left[\mathrm{d}\mu_i + \sum_j \left(\frac{\partial Y_j}{\partial n_i} \right) \mathrm{d}X_j \right] = 0 \qquad (18)$$

Comparing this equation with the classical Gibbs–Dehum equation (1), a generalized chemical potential can be defined as

$$\mathrm{d}\mu_i' = \mathrm{d}\mu_i + \sum_j \left(\frac{\partial Y_j}{\partial n_i} \right) \mathrm{d}X_j \qquad (19)$$

In this equation, the last term represents the contributions from external fields, its physical meaning is the increase in energy per mole produced by external field.

Specific forms of chemical potentials in external fields can be deduced from this generalized expression. For example, the differential expression of gravitational potential energy of a system with vertical height h is $\mathrm{d}W_\mathrm{g} = gh\mathrm{d}m$. The extensive quantity is mass, $\partial Y/\partial n = \partial m/\partial n \equiv M$, where M is molar mass which is a constant for a given substance. Thus, with Eq. (19), the chemical potential in the gravitational field can be expressed as $\mu' = \mu + Mgh$, which is also called as gravitational chemical potential [1,23]. The vertical distribution of the atmosphere can be effectively explained with this expression.

The electric potential energy of charged particles in an electric field is $\mathrm{d}W_\mathrm{e} = \phi\mathrm{d}q$. $\partial q/\partial n_i = N_\mathrm{A}z_i e = Fz_i$, where z_i is the number of elementary charge of a particle, N_A is Avogadro's number, and $F \equiv N_\mathrm{A}e$ is Faraday constant. So the chemical potential of the charged particles in an electric field can be obtained from Eq. (19), which is $\mu_i' = \mu_i + Fz_i\phi$. This equation is also known as electrochemical potential, which is the foundation of study of electrochemical equilibrium [1,24]. The other specific forms of chemical potential with the influence of external field can also be derived from this generalized expression with this same method.

4 Conclusions

Thermodynamic system may experience the actions of external fields, and the influences of external fields could be captured by thermodynamic equations. Gibbs–Duhem equation is one of the fundamental equations in thermodynamics, and it was extended to include the properties of external fields. This extended equation reveals the relation among the differentials of temperature, pressure, chemical potential, and external fields; this relation means that external fields can affect the thermodynamic properties. The influences of temperature and electric field on surface tension were understood with the extended Gibbs–Duhem equation, surface tension decreases with temperature, and with the square of electric field, respectively. Gibbs adsorption equation is extended to include the influence of electric field, which shows that electric field can enhance the surface adsorption. A generalized chemical potential was also derived with this extended Gibbs–Duhem equation, and the specific forms of chemical potential can be deduced from it. Thus, this extended Gibbs–Duhem equation is helpful to understand the behaviors of thermodynamic system acted by external fields.

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