Thermodynamics of phase transitions and chemical reactions in the presence of quasistatic electromagnetic fields

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Phase transitions and chemical reactions in the presence of electromagnetic fields are considered. The field-dependent differential of the internal energy is described using four basic independent terms. These terms stand for the differentials of heat $\hat{T}dS$, mechanical work $-\hat{P}dV$, work associated with mass transfer $\hat{\zeta}dN$, and work delivered by the current source $V\mathbf{H} \cdot d\mathbf{B}$. In this context, the field-dependent temperature $\hat{T}$, pressure $\hat{P}$, and chemical potential $\hat{\zeta}$ are the intensive conjugates of the field-independent entropy S, volume V, and mass N, respectively. In this context isothermal and isobaric processes in the presence of the field must satisfy the condition of fixed $\hat{T}$ and fixed $\hat{P}$, respectively. In an isothermal process, the heat delivered to a system where an entropy change ΔS occurs is $\hat{T}\Delta S$. Consequently, the latent heat of phase transition $\hat{l}$, which is $\hat{T}\Delta s$, is $\hat{T}/T$ times its value in the absence of the field. An extended Clausius-Clapeyron equation is derived, where the effect of the field is expressed in terms of an equivalent entropy change due to the phase transition. Different forms of mass action laws are formulated, so as to account for the effect of the field on pressures or activities of reactants and products of chemical reactions. These pressures, or activities, are modified by field-dependent factors, so that the reaction constant remains a sole function of temperature, irrespective of the presence or absence of the field. For permeable materials, these correction factors are positive, but less than unity, and their effect is to increase the corresponding pressures, or activities, above their ''field free'' equilibrium values. The van't Hoff equation for a single reaction is extended in terms of the change in the heat of reaction due to the presence of the field. Simultaneous reactions that in the absence of the field are independent, become interdependent when the field is present through their collective effect on the mixture permeability. The effect of replacing the constraint of a fixed $\mathbf{B}$ field, by a fixed $\mathbf{H}$ field, is shown to result in reversal of the effect of the field on phase transitions and chemical reactions. Finally, it is shown that on a molecular scale of paramagnetic substances such as paramagnetic ideal gases, the magnetic effect is expected to be significant at low cryogenic temperatures. At sufficiently low temperatures, this effect can become dominant. At ordinary temperatures, the field can have a dominant effect on colloidal particles having diameters of a few nanometers and larger. [S1063-651X(97)12204-8]

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INTRODUCTION

Recently the theory of thermodynamics in the presence of electromagnetic fields was formulated [1] and then followed by system analysis of field-dependent thermodynamic variables and Maxwell relations [2]. This theory provides formulations of different field-dependent intensive and extensive variables that also depend on constraints imposed on the field. Each of these field-dependent intensive variables was defined as the partial derivative of the field-dependent energy with respect to its conjugate extensive variable. In contrast to conventional, field free, thermodynamics, the field-dependent energy possesses the property that it can exist within and outside physical boundaries of a thermodynamic system. This is true, provided that the latter is the source of the field, where the energy is stored. These unique properties of thermodynamics in the presence of fields must be reflected also in the transfer of energy as heat, mechanical work, and mass and in the laws of phase transitions and chemical reactions. In this work the characteristics of phase transitions, regarding latent heat and the Clausius-Clapeyron equation, and chemical reactions in the presence of fields are formulated.

THEORY

In what follows, we set the grounds for the development of the theory of phase transition and chemical reactions in the presence of quasistatic electromagnetic fields. To this end, we first recapitulate formulations and physical meanings of field-dependent variables, and then use them for analysis of phase transitions and chemical reactions.

A. Field-dependent variables

The following theory concerns systems in the presence of magnetic fields. The differential of the field-dependent internal energy, $\hat{U}$, is given by [1]

$$d\hat{U} = \sum_{i=0}^{n} \xi_i \, dX_i + dU_M, \qquad (1)$$

where

$$\xi_i = (\partial U / \partial X_i)_{X_j}, \quad i \neq j, \quad i,j = 0,\ldots,n, \qquad (2)$$

X_i is the ith, field-independent, extensive variable, $U = \hat{U}(\mathbf{H}=0)$ is the energy in the absence of the field, and U_M is the magnetic energy.

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$$U_M = \int_{V'} \int_0^{\mathbf{B}} \mathbf{H} \cdot d\mathbf{B} dV', \tag{3}$$

$$\mathbf{B} = \mu \mathbf{H}, \tag{4}$$

where $\mathbf{H}$ and $\mathbf{B}$ are the magnetic field strength and magnetic induction, respectively, and μ is magnetic permeability. The volume V' spans the entire field and in the general case it extends to infinity, so as to include the whole space. If, as a special case, the magnetic field is confined to a volume V where $\mathbf{H}$ and μ are uniform and μ is independent of $\mathbf{H}$, then

$$U_M = \tfrac{1}{2} V \mathbf{H} \cdot \mathbf{B} = \tfrac{1}{2} V \mu H^2 = \tfrac{1}{2} V B^2 / \mu. \tag{5}$$

Suppose [1] U_M is a function of a set consisting of m'' variables Y_m, $m = 1,\ldots,m''$,

$$U_M = U_M(Y_1, Y_2, \ldots, Y_{m''}). \tag{6}$$

Suppose further that this set can be separated into two independent subsets. In the first subset, which consists of $m' - 1$ functions, Y_m, $m = 1,\ldots,m' - 1$, is dependent only on the current sources of the field, and consequently it is independent of the system variables X_i. In the second subset, the $m'' - m' + 1$ functions, Y_m, $m = m',\ldots,m''$, which are given by

$$Y_m = Y_m(X_0,\ldots,X_n), \tag{7}$$

are independent of the current sources of the field. Thus the differential of U_M can be expanded as follows:

$$dU_M = \sum_{m=1}^{m'-1} (\partial U_M / \partial Y_m) dY_m$$
$$+ \sum_{m=m'}^{m''} (\partial U_M / \partial Y_m) \sum_{i=0}^{n} \frac{\partial Y_m}{\partial X_i} dX_i, \tag{8}$$

where the partial derivatives are taken, holding all other variables (on which the function depends) fixed.

Combining Eqs. (1) and (8) gives

$$d\hat{U} = \sum_{i=0}^{n} \hat{\xi}_i dX_i + \sum_{m=1}^{m'-1} (\partial U_M / \partial Y_m) dY_m, \tag{9}$$

$$\hat{\xi}_i = \xi_i + \sum_{m=m'}^{m''} \frac{\partial U_M}{\partial Y_m} \frac{\partial Y_m}{\partial X_i}, \tag{10}$$

where

$$\hat{\xi}_i = (\partial \hat{U} / \partial X_i)_{X_j, Y_m}, \quad i \neq j,$$

$$i,j = 0,\ldots,n, \quad m = 1,\ldots,m' - 1 \tag{11}$$

and U_M is given by Eq. (3). Suppose the volume of a magnetized system is V. In the general case, V and V' differ as the field, due to the contents of V, can extend beyond the system boundaries.

The magnetic energy U_M, as given by Eq. (3), in conjunction with Eq. (4), is a function of the field vectors $\mathbf{H}$ and $\mathbf{B}$ and the way they are distributed in space. By the laws of electromagnetism, this distribution of the field depends on the boundaries of the system, i.e., on its geometry and volume V. It follows that U_M is a function of the permeability, μ, field (either $\mathbf{H}$ or $\mathbf{B}$), volume V, and the geometry of the system. This implies that, apart from the field, the surroundings of the system are invariable. In a single component isotropic and homogeneous system, the permeability is a function of the temperature T, density ρ, and field $\mathbf{H}$,

$$\mu = \mu(\rho, T, \mathbf{H}). \tag{12}$$

The temperature is a function of the entropy S, volume V, and mass N of the system

$$T = T(S, V, N), \tag{13}$$

and ρ is given by

$$\rho = N/V. \tag{14}$$

It follows that

$$\mu = \mu(S, V, N, \mathbf{H}). \tag{15}$$

If the geometry of the system is fixed, then the magnetic energy becomes a function of S, V, and N and the field (i.e., either $\mathbf{H}$ or $\mathbf{B}$). It is convenient to choose $\mathbf{B}$ as the independent field vector. This gives

$$U_M = U_M(S, V, N, \mathbf{B}). \tag{16}$$

Note that the set $S, V, N, \mathbf{B}$ can be separated into two independent subsets. The first subset includes field-independent variables only, and as such it reflects the field-independent thermodynamic properties of the system. This subset is S, V, N and, in general notation, it is presented as $X_0,\ldots,X_n$. The second subset, i.e., $\mathbf{B}$, stands here for the independent effect of the current sources. Replacing the subset, S, V, N, in Eq. (10), by the general notation of $X_0,\ldots,X_n$ gives

$$U_M = U_M(X_0,\ldots,X_n, \mathbf{B}), \tag{17}$$

$$dU_M = \sum_{i=0}^{n} (\partial U_M / \partial X_i)_{X_j} dX_i + (\partial U_M / \partial \mathbf{B})_{X_j} d\mathbf{B},$$

$$i \neq j, \quad i,j = 0,\ldots,n. \tag{18}$$

Comparing Eqs. (8) and (18) shows that, as expected,

$$(\partial U_M / \partial X_i) = \sum_{m=m'}^{m''} (\partial U_M / \partial Y_m)(\partial Y_m / \partial X_i), \tag{19}$$

$$\sum_{m=1}^{m'-1} (\partial U_M / \partial Y_m) dY_m = (\partial U_M / \partial \mathbf{B})_{X_j} d\mathbf{B}. \tag{20}$$

Equation (20) implies that $\mathbf{B}$ can be the result of the action of several (i.e., $m' - 1$) current sources. We proceed now to formulate the field-dependent intensive variables, which, similar to those prevailing in the absence of the field, are the

conjugates of S, V, and N. We assume that the properties of the system allow U_M to be presented as a function of **B**, V, and μ:

$$U_M = U_M(\mathbf{B}, V, \mu). \tag{21}$$

In accordance with the convention specified in the definition of Eqs. (6) and (7), here we have $Y_1 = \mathbf{B}$, $Y_2 = V$, $Y_3 = \mu$, and $m' = 2$, $m'' = 3$. Following Eq. (15), μ is a function of S, V, N, and **H**, so that for evaluation of Eq. (10), $X_0 = S$, $X_1 = V$, and $X_2 = N$ are used. Thus, from Eq. (10), for $i = 1$, $\hat{\xi}_1 = \hat{T}$, and $\xi_1 = T$,

$$\hat{T} = T + (\partial U_M / \partial \mu)_{V,\mathbf{B}} (\partial \mu / \partial S)_{V,N,\mathbf{H}} \tag{22}$$

for $i = 2$, $\hat{\xi}_2 = -\hat{P}$, and $\xi_2 = -P$,

$$-\hat{P} = -P + (\partial U_M / \partial V)_{\mu,\mathbf{B}} + (\partial U_M / \partial \mu)_{V,\mathbf{B}} (\partial \mu / \partial V)_{S,N,\mathbf{H}}. \tag{23}$$

For $i = 3$, $\hat{\xi}_3 = \hat{\zeta}$, and $\xi_3 = \zeta$,

$$\hat{\zeta} = \zeta + (\partial U_M / \partial \mu)_{V,\mathbf{B}} (\partial \mu / \partial N)_{S,V,\mathbf{H}}. \tag{24}$$

Equations (23) and (24) were derived in an equivalent form elsewhere [1]. We focus our interest on Eq. (22) for further development of heat related energy changes in the presence of the field. Note that had we selected **H** instead of **B** as the field vector in Eq. (21), Eqs. (22)–(24) would have been different [1].

For systems that are uniformly magnetized, using Eqs. (22)–(24) and the fact that $Y_1 = \mathbf{B}$, Eq. (9) takes the following form:

$$d\hat{U} = \hat{T} dS - \hat{P} dV + \hat{\zeta} dN + \int_{V'} \mathbf{H} \cdot d\mathbf{B} \, dV'. \tag{25}$$

Note that the last term on the right-hand side of Eq. (25) stands for the work done by the current source in establishing the field at fixed S, V, and N. If $V' = V$, and the complete field is uniform and confined within the boundaries enclosing the system, then Eq. (25) reduces to the following simpler form [3]:

$$d\hat{U} = \hat{T} dS - \hat{P} dV + \hat{\zeta} dN + V\mathbf{H} \cdot d\mathbf{B}. \tag{26}$$

The physical significance of the terms specified in Eq. (26) is discussed elsewhere [3]. However, due to the importance of understanding the utility of each of these terms, e.g., regarding phase transitions and chemical reactions, their meaning is reiterated here. Equations (25) and (26) specify four types of terms that have a clear thermodynamic meaning. The first term stands for the energy differential that is a function of the field-independent entropy S, with the field-dependent temperature $\hat{T}$ as the integration factor. At fixed volume V, mass N, and field **B** the only energy change can be due to a change in heat. This shows that, in the presence of the field, the term $\hat{T} dS$ is indeed the heat differential. In the absence of the field $\hat{T} = T$ and the conventional heat differential, i.e., $T dS$, prevails. The second term stands for the field-dependent mechanical energy differential that is a function of the field-independent volume V, with the field-dependent

pressure $\hat{P}$ as the integration factor. At fixed entropy S, mass N, and field **B**, the only energy change can be due to mechanical work sources. This shows that, in the presence of the field, the term $-\hat{P} dV$ is indeed the mechanical work differential. In the absence of the field $\hat{P} = P$ and the conventional pressure-volume work differential is obtained. The third term denotes the field-dependent energy differential due to mass transfer. It is a function of the field-independent mass N, with the field-dependent chemical potential $\hat{\zeta}$ as the integration factor. At fixed entropy S, volume V, and field **B**, the only energy change can be due to mass transfer. This shows that in the presence of the field, the term $\hat{\zeta} dN$ is indeed the mass transfer energy differential. The fourth term has been already defined as the work delivered by the current sources in magnetizing the system, at fixed entropy S, volume V, and mass N. Assuming that the geometry of the system is also fixed, the fourth term represents the energy change due to the magnetization of the system, provided that its field independent variables are held fixed during this magnetization process.

Recognizing the significance of the intensive field-dependent variables $\hat{\xi}_i$, and that their role in the presence of the field is the same as that of ξ_i in its absence, the conditions of equilibrium are that $\hat{\xi}_i$ be uniform [1]. In particular, $\hat{\xi}_i$ must be the same across unconstrained interfaces, separating two systems that are at equilibrium.

This gives rise to a jump in ξ_i across the interface. From Eq. (10) this jump is given by

$$\Delta \xi_i = -\Delta \sum_{m=m'}^{m''} (\partial U_M / \partial Y_m)(\partial Y_m / \partial X_i). \tag{27}$$

The jump in T, P, and ζ, across interfaces at equilibrium in the presence of a fixed **B** field, are readily obtained from Eqs. (22)–(24) by imposing fixed values of $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ across these interfaces. Upon removal of the field, these jumps act to change the position of the interface and drive heat and mass across them [3]. The reverse, i.e., regarding the effect of imposing a field on systems at equilibrium, is also true. In the presence of the field, isothermal and isobaric processes are defined here, as those that are carried out at fixed $\hat{T}$ and fixed $\hat{P}$, respectively. It follows that such processes can exist at variable T and P, and vice versa.

B. Field-dependent heat and latent heat

Permeable materials are characterized by $(\partial \mu / \partial S)_{V,N,\mathbf{H}} < 0$. Using the fact that $(\partial U_M / \partial \mu)_{V,\mathbf{B}} < 0$, we obtain, at fixed **B**, $\hat{T} > T$, and the effect of the field is to increase the temperature. It follows that for systems at equilibrium (or rather quasistatic equilibrium) in the presence of the field, the change in heat Q due to a change in entropy S at fixed $\hat{T}$, is given by

$$\Delta Q = \hat{T} \Delta S. \tag{28}$$

This is also true for processes of phase transitions in the presence of the field, where $\Delta Q / N$ is the corresponding latent heat $\hat{l}$:

$$\hat{l} = \hat{T}\Delta s, \tag{29}$$

$$s = S/N. \tag{30}$$

In the absence of the field the latent heat is

$$l = T\Delta s. \tag{31}$$

Combining Eqs. (29) and (31) gives

$$\hat{l} = l\hat{T}/T. \tag{32}$$

Substitution of $\hat{T}$ from Eq. (22) in Eq. (32) gives

$$\hat{l} = l + (l/T)(\partial U_M/\partial\mu)_{V,\mathbf{B}}(\partial\mu/\partial S)_{V,N,\mathbf{H}}. \tag{33}$$

It follows that if the system is permeable, then $\hat{l} > l$, and the presence of the field causes an increase in the latent heat, e.g., as compared to its value at $\mathbf{H} = \mathbf{0}$.

If Eq. (5) applies then

$$(\partial U_M/\partial\mu)_{V,\mathbf{B}} = -\tfrac{1}{2}VB^2/\mu^2 = -\tfrac{1}{2}VH^2 \tag{34}$$

and in this case, using Eqs. (14) and (30), Eq. (33) reduces to

$$\hat{l} = l - \frac{l}{2\rho T}H^2(\partial\mu/\partial s)_{V,N,\mathbf{H}} = l - \frac{1}{2\rho}H^2\Delta s(\partial\mu/\partial s)_{V,N,\mathbf{H}}. \tag{35}$$

In the presence of a fixed $\mathbf{B}$ field, the extra latent heat expresses the heat used to build up the field when the permeability decreases with an increase in the entropy S. The field is also expected to affect the Clausius-Clapeyron equation, which is derived next.

C. The Clausius-Clapeyron equation—dependence on field

The chemical potential in the presence of the field can be expressed as [see Eq. (24)]

$$\hat{\zeta} = \zeta + \zeta_M, \tag{36}$$

where ζ_M is given by the magnetic term on the right-hand side of Eq. (24).

If Eq. (5) applies, then at fixed $\mathbf{B}$,

$$\zeta_M = -\tfrac{1}{2}H^2(\partial\mu/\partial\rho)_{S,V}. \tag{37}$$

Differentiating Eq. (36) gives

$$d\hat{\zeta} = d\zeta + d\zeta_M = -s\,dT + v\,dP + d\zeta_M, \tag{38}$$

where here use was made of the Gibbs-Duhem equation in the absence of the field, and $v = V/N$ is the molar volume. Equation (38) can be applied to one phase on the P versus T phase transition curve. Similarly, for the other phase (denoted by subscript 1) at the same point,

$$d\hat{\zeta}_1 = d\zeta_1 + d\zeta_{M1} = -s_1dT + v_1dP + d\zeta_{M1}. \tag{39}$$

Subtraction of Eq. (39) from Eq. (38) gives

$$(s_1 - s)dT - (v_1 - v)dP - d(\zeta_{M1} - \zeta_M) = 0, \tag{40}$$

where here use was made of the fact that along the P versus T transition curve, $d\hat{\zeta} = d\hat{\zeta}_1$ must be satisfied.

Solving Eq. (40) for dP/dT and using Eq. (31) gives

$$dP/dT = \Delta s/\Delta v - \Delta(d\zeta_M/dT)/\Delta v$$
$$= l/T\Delta v - \Delta(d\zeta_M/dT)/\Delta v, \tag{41}$$

where

$$\Delta s = s_1 - s, \quad \Delta v = v_1 - v,$$

$$\Delta(d\zeta_M/dT) = d\zeta_M/dT - d\zeta_{M1}/dT,$$

$$d\zeta_M/dT = d[(\partial U_M/\partial\mu)_{V,\mathbf{B}}(\partial\mu/\partial N)_{S,V,\mathbf{H}}]/dT. \tag{42}$$

If the system is magnetically linear and Eq. (37) applies, then $\mu = \mu(\rho,T)$, and since $\mathbf{B}$ is fixed,

$$\zeta_M = \zeta_M(\rho,T) \tag{43}$$

and hence

$$d\zeta_M = (\partial\zeta_M/\partial\rho)_T d\rho + (\partial\zeta_M/\partial T)_\rho dT,$$
$$d\zeta_M/dT = (\partial\zeta_M/\partial\rho)_T d\rho/dT + (\partial\zeta_M/\partial T)_\rho. \tag{44}$$

If the permeability is a linear function of the density ρ, as is the case with materials such as ideal gases [3] that follow the Langevin equation, then

$$\mu = K\rho + \mu_0, \quad K = K(T), \tag{45}$$

where, at fixed temperature, K is a constant, and μ_0 is permeability of free space. In this case, $(\partial\mu/\partial\rho)_{S,V} = K$ and Eq. (37) takes the following form:

$$\zeta_M = -\tfrac{1}{2}B^2K/\mu^2. \tag{46}$$

Hence

$$(\partial\zeta_M/\partial T)_\rho = \frac{1}{2\rho}H^2(1 - 2\mu_0/\mu)(\partial\mu/\partial T)_\rho, \quad \mathbf{H} = \mathbf{B}/\mu, \quad \mathbf{B} \text{ is fixed}, \tag{47}$$

$$(\partial\zeta_M/\partial\rho)_T = \frac{1}{\rho^2}H^2(\mu - \mu_0)^2/\mu, \quad \mathbf{H} = \mathbf{B}/\mu, \quad \mathbf{B} \text{ is fixed}. \tag{48}$$

Substitution of Eqs. (47) and (48) in Eq. (44) and then the result in Eq. (41) gives

$$dP/dT = \frac{l}{T\Delta v} - \frac{B^2}{\Delta v}\Delta\left[\frac{(\mu - \mu_0)^2}{\rho^2\mu^3}\frac{d\rho}{dT} + \frac{1 - 2\mu_0/\mu}{2\rho\mu^2}\left(\frac{\partial\mu}{\partial T}\right)_\rho\right], \quad \mathbf{B} \text{ is fixed}. \tag{49}$$

Equations (41) and (49) show that the slope of the P versus T phase transition curve, in the presence of the field, is different than the one prevailing in its absence. Accordingly, the field is expected to produce a shift in the equilibrium, P versus T curve of phase transition. The ability to control the field with a great degree of precision suggests that it can be used for "fine tuning" of phase transition processes such as crystallization. In this context the field can be used for fast precision adjustment of the pressure and temperature of the phase transition process. This is due to the fact that the effect of the field is practically instantaneous. The effect of the field on the chemical potential must also be reflected in other equilibrium systems. In particular, this applies to equilibrium of chemical reactions that is discussed in the following section.

D. Chemical reactions

1. Single reaction

For a chemical reaction that is given by

$$\sum_{i=1}^{n} \nu_i A_i = 0, \qquad (50)$$

the condition of chemical equilibrium between the n reacting species can be presented as [4–6]

$$\sum_{i=1}^{n} \nu_i \zeta_i = 0, \qquad (51)$$

where A_i, ν_i, and ζ_i are the number of moles, stoichiometric coefficient, and chemical potential of the ith reacting species, $i = 1,\ldots,n$.

In the presence of fields, the same condition can be used by replacing ζ_i with $\hat{\zeta}_i$. In this case we have

$$\sum_{i=1}^{n} \nu_i \hat{\zeta}_i = 0. \qquad (52)$$

We consider first ideal gaseous systems, where the ith chemical potential in the absence of fields, ζ_i, is given by

$$\zeta_i = \zeta_{0i} + RT \ln P_i. \qquad (53)$$

By virtue of Eq. (24),

$$\hat{\zeta}_i = \zeta_{0i} + RT \ln P_i + (\partial U_M / \partial \mu)_{V,\mathbf{B}} (\partial \mu / \partial N_i)_{S,V,\mathbf{H}}. \qquad (54)$$

If Eq. (5) applies, which is expected to be true for ideal gaseous systems, then

$$\hat{\zeta}_i = \zeta_{0i} + RT \ln P_i - \tfrac{1}{2} H^2 (\partial \mu / \partial \rho_i)_{S,V}. \qquad (55)$$

Combining Eqs. (52) and (55) gives

$$-RT \ln \prod_{i=1}^{n} P_i^{\nu_i} = \sum_{i=1}^{n} \nu_i [\zeta_{0i} - \tfrac{1}{2} H^2 (\partial \mu / \partial \rho_i)_{S,V}]. \qquad (56)$$

In the absence of the field, i.e., at $\mathbf{H} = \mathbf{0}$, the sum $\sum_{i=1}^{n} \nu_i \zeta_{0i}$ is dependent on temperature but not on pressure.

This facilitates the well-known formulation of the equilibrium, or mass action, constant K_p as

$$-RT \ln K_p = \sum_{i=1}^{n} \nu_i \zeta_{0i}. \qquad (57)$$

This leads to the following mass action law [4–6]:

$$K_p = \prod_{i=1}^{n} P_i^{\nu_i} \qquad (58)$$

However, in the presence of the field the sum on the right-hand side of Eq. (56) is no longer independent of the pressure and composition of the reacting mixture. This is due to the fact that at fixed $\mathbf{B}$, $\mathbf{H}$ is an inverse function of μ, and μ is a function [see Eq. (12)] of the pressure (via the density), as well as composition of the reacting mixture. It follows that, in principle, Eq. (58) cannot be used in the conventional way in the presence of the field. This difficulty can be circumvented by modifying the pressure through manipulation of Eq. (56) as follows:

$$-RT \ln \prod_{i=1}^{n} \left\{ P_i \exp\left[-\frac{1}{2RT} H^2 (\partial \mu / \partial \rho_i)_{S,V} \right] \right\}^{\nu_i}$$

$$= \sum_{i=1}^{n} \nu_i \zeta_{0i}, \qquad (59)$$

and the field-dependent mass action law becomes

$$K_p = \prod_{i=1}^{n} \left\{ P_i \exp\left[-\frac{1}{2RT} H^2 (\partial \mu / \partial \rho_i)_{S,V} \right] \right\}^{\nu_i}. \qquad (60)$$

Comparing Eqs. (60) and (58) shows that the effect of the field can be accounted for by applying a field-dependent correction factor on the pressure P_i, $i = 1,\ldots,n$. In this way K_p retains its previous meaning, which requires independence of pressure, and composition, of the reacting mixture.

If Eq. (45) applies to the ith component of the reacting mixture, then Eq. (60) can readily be shown to take the following form:

$$K_p = \prod_{i=1}^{n} \left\{ P_i \exp\left[-\frac{\mu_0 \mathbf{H} \cdot \mathbf{M}_i}{2 \rho_i RT} \right] \right\}^{\nu_i}, \quad \mu_0 \mathbf{M}_i = (\mu_i - \mu_0) \mathbf{H}, \qquad (61)$$

where $\mathbf{M}_i$ is magnetization of the ith reacting species. Equation (61) shows that the field-dependent correction factor is exponentially dependent on the ratio of the magnetic energy density (e.g., per unit mass of substances such as ideal gases) and its translational component of the thermal energy density. Recall the convention that negative values of ν_i are assigned to reactants and positive ones to the reaction products.

Since at fixed temperature K_p is also fixed, the condition that the field will have no effect on the product of the equilibrium pressures P_i is obtained by setting the variable α (as defined below) to zero:

$$\sum_{i=1}^{n} \nu_i \mu_0 \mathbf{H} \cdot \mathbf{M}_i / (2\rho_i RT) = \alpha = 0. \qquad (62)$$

If $\alpha > 0$, then $\Pi_{i=1}^{n} P_i^{\nu_i}$ must be larger than its value at $\mathbf{H} = \mathbf{0}$, so that K_p is maintained fixed and independent of the pressure. This means that the reaction is enhanced by the field toward the products. The reverse is true if α is negative. The physical implication of this effect of the field can be described in terms of response of the system to field-related energy changes. If $\alpha > 0$, then the overall negative magnetic energy change due to the reaction provides an additional driving force, which shifts the equilibrium further, so that more products are produced. The reverse applies for the case of $\alpha < 0$. Note that had we started the analysis with Eq. (54) instead of Eq. (55), the outcome would have been the same, but of a more general nature.

If a reacting mixture is not ideal, and as such possesses imperfect properties, then the mass action constant can be expressed in terms of activities a_i rather than P_i, and the counterpart of Eq. (61) is readily obtained as

$$K_a = \prod_{i=1}^{n} \left\{ a_i \exp\left[-\frac{\mu_0 \mathbf{H} \cdot \mathbf{M}_i}{2\rho_i RT} \right] \right\}^{\nu_i}, \qquad (63)$$

where K_a is the mass action constant expressed in terms of activities of the reactants and products. Similarly, replacing the activities in Eq. (63) by mole fractions yields a mass action constant in terms of mole fractions of the species of the reacting mixture.

Note that Eq. (63) has a wider scope in the sense that it can be applied to reactions in all three phases, e.g., gas, liquid, and solid. The significance of the magnetic correction factor is enhanced when the field strength is increased, the temperature is decreased, and for materials having higher molar magnetic moment. Numerical examples that are illustrated in the Appendix show that at the current available field strength, the magnetic correction factor (which is also linked to the latent heat of phase transition) is significant in the cryogenic region, where it can become dominant if the temperature is sufficiently lowered. The presentation of the mass action law in the form of Eqs. (60), (61), and (63) facilitates the use of van't Hoff's equation for evaluation of the temperature dependence of K_p. This is due to the fact that, in these equations, K_p retains its original meaning, and hence it can be treated using conditions that prevail in the absence of the field. This also facilitates the use of the standard free energy of the reaction for evaluation, in the conventional way, of K_p, and vice versa. The van't Hoff equation is given by

$$d \ln K_p / dT = \Delta H / RT^2, \qquad (64)$$

where ΔH is the heat of reaction in the absence of the field. The heat of reaction in the presence of the field is expected to be different from ΔH, since it must account for the field-dependent changes in heat that are the outcome of the reaction. In what follows, we derive the field-dependent heat of reaction. We transform Eq. (1) so as to obtain the counterpart of the differential of the Gibbs function in the presence of magnetic fields:

$$d(\hat{U} - TS + PV) = d\hat{G} = -SdT + VdP + \zeta dN + dU_M. \qquad (65)$$

We stipulate that, for continua, the dependence of U_M on S, V, N, and $\mathbf{B}$ [see Eq. (16)] can be transformed to an equivalent dependence on T, P, N, and $\mathbf{B}$.

In this case

$$dU_M = (\partial U_M / \partial T)_{P,N,\mathbf{B}} dT + (\partial U_M / \partial P)_{T,N,\mathbf{B}} dP$$
$$+ (\partial U_M / \partial N)_{T,P,\mathbf{B}} dN + (\partial U_M / \partial \mathbf{B})_{T,P,N} d\mathbf{B}. \qquad (66)$$

Combining Eqs. (65) and (66) gives

$$d\hat{G} = -[S - (\partial U_M / \partial T)_{P,N,\mathbf{B}}] dT + [V + (\partial U_M / \partial P)_{T,N,\mathbf{B}}] dP$$
$$+ [\zeta + (\partial U_M / \partial N)_{T,P,\mathbf{B}}] dN + [(\partial U_M / \partial \mathbf{B})_{T,P,N}] d\mathbf{B}. \qquad (67)$$

It follows that

$$\{\partial [\zeta + (\partial U_M / \partial N)_{T,P,\mathbf{B}}] / \partial T\}_{P,N,\mathbf{B}}$$
$$= -\{\partial [S - (\partial U_M / \partial T)_{P,N,\mathbf{B}}] / \partial N\}_{T,P,\mathbf{B}}. \qquad (68)$$

However, due to the fact that U_M is a state function and dU_M is an exact differential, we have

$$[\partial (\partial U_M / \partial N)_{T,P,\mathbf{B}} / \partial T]_{P,N,\mathbf{B}} = [\partial (\partial U_M / \partial T)_{P,N,\mathbf{B}} / \partial N]_{T,P,\mathbf{B}} \qquad (69)$$

and hence, as expected,

$$(\partial \zeta / \partial T)_{P,N,\mathbf{B}} = -(\partial S / \partial N)_{T,P,\mathbf{B}} \qquad (70)$$

holds once again irrespective of the presence of the field. Equation (70) leads to Eq. (64). However, in the presence of the field K_p can be presented as a field-dependent reaction parameter [see Eqs. (56)–(58), where the original, unmodified, field-independent pressures are used to define K_p]. This gives

$$-RT \ln K_p + \sum_{i=1}^{n} \nu_i \frac{1}{2} H^2 (\partial \mu / \partial \rho_i)_{S,V} = \sum_{i=1}^{n} \nu_i \zeta_{0i}. \qquad (71)$$

As the right-hand side of Eq. (71) is a sole function of temperature, the left-hand side of this equation must also possess this property. Differentiating both sides of Eq. (71) with respect to T and rearranging gives

$$RTd \ln K_p / dT$$
$$= \left\{ \Delta H + Td \left[\sum_{i=1}^{n} \nu_i \frac{1}{2} H^2 (\partial \mu / \partial \rho_i)_{S,V} \right] \bigg/ dT \right\} \bigg/ T. \qquad (72)$$

If Eq. (45) applies, then Eq. (72) takes the following form:

$d \ln K_p / dT$

$$= \left[\Delta H + T d \left(\sum_{i=1}^{n} \nu_i \mu_0 \mathbf{H} \cdot \mathbf{M}_i / 2\rho_i \right) \middle/ dT \right] \middle/ RT^2. \tag{73}$$

It is necessary to verify first that the terms involving sums of magnetic energy densities in Eqs. (72) and (73) indeed represent heat interaction with the field. This is true due to the fact that at fixed $\mathbf{B}$ (which here implies also fixed flux linkage at the current sources), no energy exchange between the field and its current sources can occur. Furthermore, since the reaction takes place at fixed pressure within a uniform field as part of a continuum, no mechanical interactions with external sources that involve the field exist. This leaves field-heat interactions as the only outcome of the reaction that involves changes in the energy of the field. Equations (72) and (73) show that, at $\mathbf{H} > \mathbf{0}$, if the temperature derivative of the change in the magnetic part of the chemical potential, due to the reaction, is positive, then the heat of reaction is expected to be larger than that at $\mathbf{H} = \mathbf{0}$. In this context, at fixed $\mathbf{B}$, if upon completion of the reaction, a decrease in the magnetic energy density of the mixture occurs (which is larger in magnitude than any work that might have been delivered, by the field, to external mechanical sources), then heat is released by the field due to this reaction. This field-dependent heat becomes part of the heat of reaction. If, during the reaction at fixed $\mathbf{B}$, no work is delivered by the field to external mechanical sources, then the entire change in the field energy of the mixture turns into the field-dependent heat of reaction. The reverse is true when the energy of the field builds up due to the reaction. This buildup of field energy is expected to draw on the heat sources of the system, thus reducing the heat available from exothermic reactions.

Hitherto we have considered single reactions. The effect of the field on simultaneous reactions and their interdependence is considered next.

2. Simultaneous reactions

In the absence of the field, if there exist j' independent reactions that take place simultaneously, then the equilibrium of the jth reaction $j = 1, \ldots, j'$, that involves a total of n_j reacting components, is given by

$$\sum_{i=1}^{n_j} \nu_{ji} \zeta_{ji} = 0, \quad j = 1, \ldots, j', \quad i = 1, \ldots, n_j. \tag{74}$$

In the presence of the field the counterpart of Eq. (74) is obtained by replacing ζ_{ji} with $\hat{\zeta}_{ji}$. The result is

$$\sum_{i=1}^{n_j} \nu_{ji} \hat{\zeta}_{ji} = 0. \tag{75}$$

However, in the presence of the field the reactions are no longer independent. This is a consequence of variability of permeability, and magnetic energy, with composition of the mixture as the reactions proceed.

The mass action law for each reaction can be presented in one of the forms given by Eqs. (60), (61), and (63). In this way the reaction constant of the jth reaction, K_{pj}, is a sole

function of temperature, and hence it retains its original ''field free'' properties. It follows, that the selection of this presentation of K_{pj} leads to interdependence of the reactions via their common field $\mathbf{H}$, e.g., through their modified pressures. At fixed $\mathbf{B}$, the field $\mathbf{H}$ is inversely proportional to μ. It is clear that in the case of a reacting mixture, μ is a function of composition, temperature, and the field. This can be expressed as follows:

$$\mu = \mu(\{\rho_{ji}\}, T, \mathbf{H}), \quad j = 1, \ldots, j', \quad i = 1, \ldots, n_j, \tag{76}$$

where $\{\rho_{ji}\}$ denotes the complete set of densities in the mixture. Equations (61) and (63) show that for mixtures that satisfy Eq. (45), the common magnetic effects of all components present in a single reaction mixture is through the field $\mathbf{H} = \mathbf{B} / \mu(\{\rho_i\}, T, \mathbf{H})$, whereas the magnetic self-effect of a specific, i.e., ith, component is through the term $\mathbf{M}_i / \rho_i$. Similarly, in simultaneous reactions, the common magnetic effect of all reacting components is through the field $\mathbf{H} = \mathbf{B} / \mu(\{\rho_{ji}\}, T, \mathbf{H})$, whereas the specific effect of the ith component of the jth reaction is through the term $\mathbf{M}_{ji} / \rho_{ji}$. Thus, the equilibrium must be found by solving the j' simultaneous equations given by Eq. (75). It is only when the effect of the field is small enough that the simultaneous reactions can be approximated as being independent. In this context, the assumption of independence of the reactions can be used as a first iteration in the solution procedure.

The theory has been presented here for the case of fixed $\mathbf{B}$ fields, which implies that no energy exchange between the system and current sources of the field exist. However, constraints other than fixed $\mathbf{B}$ can be imposed on the system. For example, the constraint of a fixed $\mathbf{B}$ field can be replaced by a fixed $\mathbf{H}$ field. This latter constraint allows energy exchange between the current sources and the system, and hence the meaning of field-dependent thermodynamic variables must change accordingly [1].

E. Fixed H fields

In fixed $\mathbf{H}$ fields, $\mathbf{B}$ is a sole function of μ; see Eq. (4). Hence, by virtue of Eqs. (15) and (16), U_M becomes a function of S, V, and N, e.g., in the sense that these are the variables whereby the magnetic energy can be changed. This can also be inferred from Eq. (21), once $\mathbf{B}$ is replaced by $\mathbf{H}$ as the independent variable. At fixed $\mathbf{H}$, U_M becomes a function of V and μ, which is equivalent to being a function of S, V, and N. Here the field-dependent thermodynamic variables retain the form given by Eqs. (22)–(24) provided that $\mathbf{B}$, in the subscripts of the partial derivatives involving U_M, is replaced by $\mathbf{H}$ as an indication that this field vector is being held fixed. Using this new field-dependent set of intensive variables, e.g., $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ at fixed $\mathbf{H}$, Eq. (26) is replaced by

$$d\hat{U}_{\mathbf{H}} = \hat{T} dS - \hat{P} dV + \hat{\zeta} dN, \quad \mathbf{H} \text{ is fixed.} \tag{77}$$

Thus, the thermodynamic significance of the field-dependent set $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$, is retained, irrespective of the selection of $\mathbf{B}$ or $\mathbf{H}$ as the fixed field. It follows that the theory developed for the case of fixed $\mathbf{B}$ fields can be applied directly to fixed $\mathbf{H}$ fields, provided that appropriate caution is exercised in ascertaining the meaning of field-dependent variables. As al-

ready mentioned, this involves replacement of **B** by **H** as the subscript indicating the variable held fixed, when the partial derivative of U_M is taken with respect to V or μ. The result is reversal of the sign of the magnetic terms. For example, if Eq. (5) applies, then

$$(\partial U_M / \partial \mu)_{V,\mathbf{H}} = -(\partial U_M / \partial \mu)_{V,\mathbf{B}}. \tag{78}$$

Hence, in this case, the effect of a fixed **H** field on $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ has the same magnitude as that of a fixed **B** field, but it is reversed. This reversal of effect is then carried over to field-dependent heat, latent heat of phase transitions, the Clausius-Clapeyron equation, and to chemical reactions. Thus, for permeable materials that have a negative rate of change of permeability with entropy, we find that at fixed **H**, $\hat{T}<T$, $\hat{\zeta}>\zeta$, $\Delta Q(\mathbf{H}>0)<\Delta Q(\mathbf{H}=0)$ [see Eq. (28)], $\hat{l}(\mathbf{H}>0)<\hat{l}(\mathbf{H}=0)$ [see Eq. (29)], $\zeta_M>0$ [see Eq. (37)]. Furthermore, the field-dependent correction factor in Eqs. (60), (61), and (63) turns larger than 1. This imposes a decrease on P_i and a_i as compared to their ''field free'' equilibrium values. The effect of reversal of sign of the magnetic terms on the heat of reaction can be considered by inspection of Eqs. (72) and (73) and their related text.

All these changes in the effect of the field are the result of interactions between the phases involved, in the phase transition process, and the current sources. The outcome of these interactions is expressed by the fact that, at fixed **H**, $\hat{T}<T$. If the phase transition involves a positive change in entropy, and consequently μ decreases as the new phase builds up at fixed $\hat{T}$, then at fixed **B**, where $\hat{T}>T$, the magnetic part of $\hat{T}$ (in the new phase) increases. This suggests that at fixed **B**, a greater part of the heat content of the new phase is stored in its magnetic field. This is associated with the occurrence of a smaller value of T in the new phase, and hence, a jump in T between the two phases develops, as expected.

At fixed **H**, where $\hat{T}<T$, a decrease in μ, due to formation of a new phase (at fixed $\hat{T}$) involves a decrease in T. Since $\hat{T}$ is fixed, this results in a decrease in the magnitude of the negative magnetic part of T, which expresses the work done by the demagnetizing field on its current sources. Similar observations can be made for chemical reactions.

The theory considered hitherto is concerned with magnetic fields. The procedure that allows the use of this theory, for the case of electroquasistatic fields, is discussed next.

F. Electroquasistatic fields

The theory developed for magnetoquasistatic fields can be applied directly to electroquasistatic fields, whenever there is an appropriate analogy between the two fields. This analogy is known to exist in cases involving materials that are polarizable by the fields. In such cases, the characteristic set of magnetic variables can be replaced by their electric counterpart, and then the theory can be applied, with the new electric variables. For example, to this end, the set **H**, **B**, μ is replaced by its electric analog **E**, **D**, ϵ (e.g., electric field strength, electric displacement, and permittivity, respectively), U_M by U_e (e.g., electric energy), and $\mu_0\mathbf{M}$ by $\mathbf{P}_E$ (e.g., electric polarization).

SUMMARY AND CONCLUSIONS

(1) The field-dependent differential of the internal energy of a single component system consists of four physically distinct and independent terms. Each of the first three terms is a product of a field-independent differential and a field-dependent integration factor. This integration factor and the variable in the differential are intensive and extensive conjugate variables, respectively. The physical significance of each of these three terms is as follows: $\hat{T}dS$, $-\hat{P}dV$, and $\hat{\zeta}dN$ are differentials of, heat, mechanical work, and work involving mass transfer, in the presence of the field, respectively. In the absence of the field, these terms reduce to the conventional heat, mechanical, and mass transfer work differentials, respectively. The fourth term stands exclusively for the work done by the current sources in establishing the field of the system at fixed entropy S, volume V, and mass N. As the field and magnetic energy of the system can be partitioned on both sides of its physical boundaries, all four terms depend on this energy and the way it is partitioned.

(2) Equilibrium requires that $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$ be uniform. Uniformity of $\hat{T}$, $\hat{P}$, and $\hat{\zeta}$, across interfaces that are shared by systems at equilibrium, can result in discontinuous jumps in the field-independent T, P, and ζ, and vice versa.

(3) In the presence of the field, isothermal and isobaric processes are defined as those satisfying the condition that $\hat{T}$ and $\hat{P}$ are fixed throughout, respectively. Such processes can involve variable T and P, and vice versa.

(4) In the presence of the field, the heat delivered to a system in an isothermal process is $\hat{T}\Delta S$. Consequently the latent heat of the phase transition is $\hat{l}=\hat{T}\Delta s$. This latent heat is $\hat{T}/T$ times the value of the ''field free'' latent heat $l=T\Delta s$.

(5) An extended Clausius-Clapeyron equation in the presence of magnetic fields has been formulated. This equation shows that the effect of the field can be presented in terms of an increase in Δs by $-\Delta (d\zeta_M/dT)$.

(6) Different forms of the mass action law in the presence of the field have been formulated. In these formulations the reaction constant retains its sole dependence on temperature as a result of use of modified pressures and activities. For the ith reacting component, the modified pressure (or activity) is defined as the product of a field-dependent factor and the field-independent pressure P_i (or activity a_i). Permeable materials are characterized by a positive factor that is less than 1. This indicates that P_i is pushed to higher equilibrium values by the field.

(7) The heat of reaction in the presence of the field has been formulated. The effect of the field is found to change the ''field free'' heat of reaction ΔH by $Td(\sum_{i=1}^{n}\nu_i\mu_0\mathbf{H}\cdot\mathbf{M}_i/2\rho_i)/dT$. Simultaneous reactions that are independent at $\mathbf{H}=\mathbf{0}$, become interdependent at $\mathbf{H}>\mathbf{0}$. This is a result of their collective effect on the permeability of the reacting mixture.

(8) The field-dependent thermodynamic variables, the heat delivered to a system, the latent heat of phase transition, the Clausius-Clapeyron equation, and chemical reactions, in the presence of the field, all depend on the constraints imposed on this field. Reversal of the effect of the field is obtained when fixed **B** fields are replaced by fixed **H** fields.

(9) The theory developed for magnetoquasistatic fields can be used for analogous cases of polarization in electroquasistatic fields, by replacing the magnetic variables with their electric analogs.

APPENDIX

The magnetic correction factor of pressure and chemical activity

The magnetic correction factor [see Eqs. (61) and (63)], for the pressure and chemical activity in the mass action law, of materials that satisfy Eq. (45) is defined by

$$\psi = \exp(-\varphi), \tag{A1}$$

where

$$\varphi = \frac{\mu_0 \mathbf{M} \cdot \mathbf{H}}{2\rho RT}, \tag{A2}$$

$$\mathbf{M} = \chi \mathbf{H}. \tag{A3}$$

For materials that satisfy the Langevin equation,

$$\chi = C/T, \tag{A4}$$

$$C = \tfrac{1}{3}\rho \widetilde{N} \mu_0 m^2 / k, \tag{A5}$$

where $\widetilde{N}$, m, and k are Avogadro's number, the dipole moment of a single molecule, and Boltzmann's constant, respectively.

Combining Eqs. (A2)–(A5) and using $R = \widetilde{N}k$ gives

$$\varphi = \beta H^2 / T^2, \tag{A6}$$

where β is a constant that depends on the dipole moment of the material,

$$\beta = \frac{1}{6}\left(\frac{\mu_0 m}{k}\right)^2. \tag{A7}$$

It follows that according to Eqs. (A6) and (A7), φ is determined by m, H, and T. Furthermore, since φ is independent of ρ, it applies to gases as well as to condensed matter that follows the Langevin equation.

For reasons of convenience, we define φ_0 (of a given material) as a reference value of φ, at $H = H_0$ and $T = T_0$ so that by virtue of Eq. (A6),

$$\varphi = \varphi_0 (H/H_0)^2 (T_0/T)^2, \quad \varphi_0 = \beta H_0^2 / T_0^2. \tag{A8}$$

The following data are used to evaluate φ_0:

$$\mu_0 = 4\pi \times 10^{-7} \text{ H/m or m kg s}^{-2}\text{ A}^{-2},$$

$$R = 8.314 \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1} \text{ mol}^{-1},$$

$$H_0 = 1/\mu_0 (\text{T/m kg s}^{-2}\text{ A}^{-2}) \text{ or A m}^{-1},$$

$$T_0 = 273.16 \text{ K}$$

$$M_0 = \chi_0 H_0 \text{ A m}^{-1}.$$

TABLE I. Calculated values of φ and ψ for the case $\chi_0 = 6.2 \times 10^{-6}$, representing an ideal gas such as oxygen.

H (T)	T (K)	φ	ψ
1	273.16	24.374×10^{-6}	1.000
2	90.00	898.12×10^{-6}	0.999
2	27.316	97.496×10^{-4}	0.990
2	2.7316	0.975	0.377
10	90.00	$22\,453 \times 10^{-6}$	0.978
10	27.316	0.24374	0.784
10	2.7316	24.374	2.597×10^{-11}
20	90.00	898.12×10^{-4}	0.914
20	27.316	0.975	0.377
20	2.7316	97.496	4.55×10^{-43}

Using Eq. (A2) for evaluation of φ_0, in conjunction with Eq. (A3) and the above data, gives

$$\varphi_0 = \frac{\chi_0/\mu_0}{2P_0}, \quad P_0 = \rho_0 RT_0. \tag{A9}$$

If the material is an ideal gas at standard conditions, then

$$\rho_0 = 1000/22.414 = 44.615 \text{ mol m}^{-3},$$

$$P_0 = 101\,323 \text{ kg m}^{-1} \text{ s}^{-2},$$

$$\varphi_0 = 3.927\chi_0. \tag{A10}$$

Suppose the reference volume susceptibility of a paramagnetic gas, such as oxygen, is $\chi_0 = 6.2 \times 10^{-6}$ and $H = 30$ T, $T = 90$ K, then using Eqs. (A8) and (A10), in conjunction with the data specified above, gives $\varphi = 0.1695$ and hence, by Eq. (A1), $\psi = 0.844$.

Table I summarizes calculated values of φ and ψ for the case $\chi_0 = 6.2 \times 10^{-6}$, representing an ideal gas such as oxygen.

Clearly the effect of the field on the ideal gas is enhanced at cryogenic temperature levels and conventional yoke magnets that produce a $2T$ field have a significant effect that is greater than 0.1% for temperatures lower than 90 K. With superconducting magnets the effect becomes larger than 2.2% in this temperature range and a $10T$ field. The dominance of the field becomes evident as the temperature is lowered below 27 K.

The comparison between two different materials can be done by evaluation of the ratio of their magnetic moment per molecule. The magnetic dipole moment m of a single molecule can be related to the magnetization as follows:

$$m = \frac{\mu_0 M w}{\rho \widetilde{N}}, \tag{A11}$$

where w is molecular weight. Hence,

$$\frac{m_2}{m_1} = \frac{M_2 w_2 / \rho_2}{M_1 w_1 / \rho_1}. \tag{A12}$$

Using Eqs. (A6) and (A7) at fixed $\mathbf{H}$ and T gives

$$\frac{\varphi_2}{\varphi_1} = \left(\frac{m_2}{m_1}\right)^2 = \left(\frac{M_2 w_2/\rho_2}{M_1 w_1/\rho_1}\right)^2 = \left(\frac{\chi_2 w_2/\rho_2}{\chi_1 w_1/\rho_1}\right)^2. \quad \text{(A13)}$$

For example, consider iron (subscript 2) and oxygen (subscript 1): $w_2 = 55.847$, $\rho_2 = 7870$ kg/m^3, $\chi_2 = 1.0$; $w_1 = 32$, $\rho_1 = 1.429$ kg/m^3, $\chi_1 = 6.2 \times 10^{-6}$.

Substitution of these data in Eq. (A13) gives $m_2/m_1 = 51.11$, $\varphi_2/\varphi_1 = 2612.35$. Since $\chi_2 = 1.0$ can be obtained from iron at a field of 2 T, we have from Table I $\varphi_1 = 898.12 \times 10^{-6}$ at 90 K, and hence at this temperature $\varphi_2 = 2.346$, $\psi_2 = 0.0958$. Increase of **H** beyond the level that is necessary to saturate the iron is expected to change φ_2 linearly with the field, since above saturation, the magnetization $\chi_2 \mathbf{H} = \mathbf{M}_2$, is fixed.

The latent heat of phase transition can be related to φ as follows: The latent heat is given by Eq. (35), and the entropy density of ideal gas by [3,5]

$$s = s_0 + \frac{3}{2} R \ln \frac{T}{T_0} + R \ln \frac{v}{v_0}, \quad v = 1/\rho. \quad \text{(A14)}$$

Hence

$$(\partial s/\partial T)_{V,N,H} = \frac{3R}{2T}, \quad \text{(A15)}$$

$$(\partial \mu/\partial s)_{V,N,H} = (\partial \mu/\partial T)_{V,N,H}/(\partial s/\partial T)_{V,N,H}$$

$$= \frac{2T}{3R}\left(\frac{\partial \mu}{\partial T}\right)_{V,N,H} = \frac{2T}{3R}\mu_0\left(\frac{\partial \chi}{\partial T}\right)_{V,N,H}$$

$$= -\frac{2\mu_0}{3R}\chi, \quad \text{(A16)}$$

where use was made of $\mu = \mu_0(1+\chi)$ and $\chi = C/T$ at fixed ρ.

Substitution of Eq. (A16) in Eq. (35) gives

$$\hat{l} = l\left(1 + \frac{\mu_0 \mathbf{M}\cdot\mathbf{H}}{3\rho RT}\right) = l\left(1 + \frac{2}{3}\varphi\right), \quad \text{(A17)}$$

where use was made of $\mathbf{M} = \chi\mathbf{H}$.

Thus, the range of temperature and field intensity where φ is significant, e.g., as regards its effect on the activity, applies also to the latent heat in the presence of magnetic fields.

The effect of magnetic fields on matter in the form of colloidal particulates is considered next. The magnetic correction factor for matter that is in the form of uniform colloidal particulates can readily be shown to take the following form:

$$\varphi = \frac{\mu_0 V_p \mathbf{M}\cdot\mathbf{H}}{2kT}, \quad \text{(A18)}$$

where V_p denotes volume of a single particulate and k is Boltzmann's constant, $k = 1.38 \times 10^{-23}$ m^2 kg s^{-2} K^{-1}.

If the properties of the particulates are such that the magnetic moment is locked in so that its direction fluctuates due to thermal agitation, then

$$\mathbf{M} = L\mathbf{M}_p, \quad L = \coth a - 1/a, \quad \text{(A19)}$$

where M_p is the locked-in magnetization and L is the Langevin function:

$$a = \mu_0 V_p \mathbf{M}_p \cdot \mathbf{H}/kT. \quad \text{(A20)}$$

Here, the counterpart of Eq. (A8) is

$$\varphi = \varphi_0 \frac{V_p L}{V_{p0} L_0}\left(\frac{H}{H_0}\right)^2\left(\frac{T_0}{T}\right)^2. \quad \text{(A21)}$$

We evaluate φ_0 with the same data used to derive Eq. (A10), and assuming spherical particulates, 10 nm in diameter. The result is as follows:

$$\varphi_0 = 55.267\chi_0.$$

For example, magnetized single domain ferromagnetic particulates have locked-in magnetic moments and when dispersed in a carrier fluid are known to follow the Langevin equation. For a 10-nm ferromagnetic particle that is characterized by $\mu_0 M = 0.56$ T at $H = 1$ T, and $T = 273.16$ K, the values of φ and ψ are $\varphi = 30.949$, $\psi = 3.623 \times 10^{-14}$. Note that due to the fact that here $L \approx 1$ the use of $\mathbf{M} = \mathbf{M}_p$ as an approximation is justified. Clearly, in this case, the magnetic effect is by far the dominant one, and it is expected to be significant also for smaller particles, e.g., of the order of a few nm.

The effect of the field is expected to be significant also in the case of colloidal paramagnetic particulates. For example, the values of φ and ψ, which are obtained by Eq. (A18), for a 10-nm particulate at $T = 90$ K, $H = 2$ T, and $\chi = 3.4 \times 10^{-3}$ are $\varphi = 2.281$, $\psi = 0.102$. If the field is increased to 10 T, then the magnetic effect remains unchanged when the diameter of the colloidal particle decreases to 3.42 nm.

In this context, consider the following reaction:

$$jA \rightarrow A_j. \quad \text{(A22)}$$

In this reaction j molecules A combine together to form a colloidal nucleus A_j, where subscript j denotes the number of molecules in A_j.

If A_j is formed in the presence of a magnetic field from a source of molecules that is maintained at fixed temperature and pressure, outside the field, then reaction (A22) can be presented as

$$\begin{array}{c} jA \rightarrow jA^f, \\ jA^f \rightarrow A_j^f, \\ \hline jA \rightarrow A_j^f, \end{array} \quad \text{(A23)}$$

where superscript f denotes the presence of the field. Equation (63) can be rearranged as follows:

$$K_p = K_{p0}\exp\left(-\sum_{i=1}^{n}\nu_i\varphi_i\right), \quad K_{p0} = K_p(\mathbf{H}=\mathbf{0}). \quad \text{(A24)}$$

Reaction (A22) specifies j identical reactants and one product. Hence, in this case, $n = j+1$, $\nu_i = -1$, $\varphi_i = \varphi_A$, $i = 1,\ldots,n-1$, $\nu_n = 1$, $\varphi_n = \varphi_{A_j}$, and Eq. (A24) gives

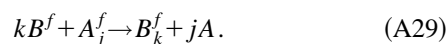$$K_p = K_{p0}\exp(j\varphi_A - \varphi_{A_j}).\qquad\text{(A25)}$$

Recall that molecules A originate from a ''field free'' source, for which $\varphi_A = 0$, and hence

$$K_p = K_{p0}\psi_{A_j},\quad \psi_{A_j} = \exp(-\varphi_{A_j}),\qquad\text{(A26)}$$

where ψ_{A_j} is the magnetic correction factor due to A_j.

Since at fixed temperature K_p is fixed, the field enhances, or retards, the reaction depending on φ_{A_j}, being positive or negative, respectively. By virtue of Eq. (A18), the increase in V_p, due to an increase in j, intensifies the effect of the field. As shown above, the effect of currently available fields can be significant down to nuclei diameter of a few nanometers.

Similar conclusions can be drawn regarding the evolution of a less permeable nucleus in a permeable medium. For example, if k molecules of a dissolved gas B associate to form a nucleus B_k that displaces an assembly of liquid molecules A_j of equal volume V_p away from the field, then a change in magnetization occurs in V_p as a result of the following reactions:

$$kB^f \rightarrow B_k^f,\qquad\text{(A27)}$$

$$\underline{A_j^f \rightarrow jA,}\qquad\text{(A28)}$$

$$kB^f + A_j^f \rightarrow B_k^f + jA.\qquad\text{(A29)}$$

Reactions (A27) and (A28) show that B molecules react in the field to produce a nucleus B_k of volume V_p, and that the assembly of liquid molecules A_j, which is displaced from V_p, is transferred outside the field as j molecules. Suppose the magnetic moment per unit volume of B is negligible as compared to that of A. For example, this condition is satisfied in a single component system where A denotes molecules in the liquid state and B stands for the same molecules in the gaseous state, so that in V_p, $k \ll j$. In this case Eq. (A24) reduces to

$$K_p = K_{p0}\exp(\varphi_{A_j})\qquad\text{(A30)}$$

and the field acts to suppress the formation of the gaseous nucleus. In view of the data given above, such suppression is expected to be significant for the case of liquid oxygen, and other permeable fluids.

This simple analysis points at potential uses of fields to prevent the evolution of imperfections in the growth processes of homogeneous and uniform phases. If the imperfection introduces differences in magnetic permeability, the field suppresses this difference, thus enhancing uniformity. The larger the imperfection and the difference in permeability, the more pronounced the field effect is expected to be.

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