Subsequent investigations, in particular of the heat transfer, would be useful in establishing the extent to which approximate methods such as the one considered herein agree with more exact solutions or experimental results. It is of note that the calculation of the heat transfer to the wall is less clear, there being numerous specifications, i.e., by being consistent with that obtained from the similarity solutions, by using the similarity solutions directly with $\bar{\beta}$ as the parameter,[4,5] by using the integral form of the energy equation,[11] or by other methods suggested for the one parameter method e.g., Hays and Probstein[12] and Chan,[13] but there is little heat transfer data to appraise the various methods in flows over a large range of speeds and accelerations such as in supersonic nozzles.

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Thermodynamics of Chemical Systems in External Fields

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RECENT experiments during space flight have accorded special importance to the thermodynamics of systems subjected to gravitational, electrical, and magnetic fields. There is considerable interest in preparing new types of materials or in processing materials in space, including regions of zero gravity in space.[1] Although formal thermodynamic treatment is available,[2,3] its application to chemical systems is obscure. It is the purpose of this paper to discuss explicitly the influence of external fields on phase equilibria, and the influence of external fields on chemical equilibria.

Thermodynamics of Equilibrium Systems

The energy change $\mathrm{d}U$ for a multicomponent system in an external field X_j, because of an infinitesimal change in χ_j at temperature T and pressure P, is given by

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + \Sigma\mu_i \mathrm{d}n_i + \Sigma X_j \mathrm{d}\chi_j \tag{1}$$

where χ_j represents the product of mass m and height z for a gravitational field, electric dipole moment for an electrical field, and magnetic dipole moment for a magnetic field. μ_i and n_i are the chemical potential and number of moles of component i, respectively. The Gibb's free energy change can be expressed in a similar manner, as follows

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + \Sigma\mu_i \mathrm{d}n_i + \Sigma X_j' \mathrm{d}\chi_j \tag{2}$$

where the j summation is over different fields.

The thermodynamics of heterogeneous equilibria for a mixture having C components, and p phases in an external field, can be easily developed, in the usual manner using Eq. (2) as the basis. When T, P, and the χ_j associated with the other fields are kept constant

$$(\mathrm{d}G)_{T,p,\chi j} = \Sigma\mu_i^1 \mathrm{d}n_i^1 + \Sigma\mu_i^2 \mathrm{d}n_i^2 + ---- + \Sigma\mu_i^p \mathrm{d}n_i^p \tag{3}$$

where the superscripts refer to the corresponding phase. At equilibrium $(\mathrm{d}G)_{T,P,\chi j} = 0$, and hence

$$\Sigma\mu_i^1 \mathrm{d}n_i^1 + \Sigma\mu_i^2 \mathrm{d}n_i^2 + ---- + \Sigma\mu_i^p \mathrm{d}n_i^p = 0 \tag{4}$$

Because of conservation of mass, one would have

$$\sum_{j=1}^{p} \mathrm{d}n_i^j = 0 \quad (\text{for } i = 1,2,3,---c) \tag{5}$$

Equation (5) combined with Eq. (4), using Lagrange's method of undetermined multipliers, yields the following $C(p\text{-}1)$ set of equations

$$\begin{array}{l} \mu_1^1 = \mu_1^2 = \mu_1^3 = \quad -------- = \mu_1^p \\ \mu_2^1 = \mu_2^2 = \mu_2^3 = \quad -------- = \eta_2^p \\ \mu_3^1 = \mu_3^2 \mu_3^3 = \quad ---------- = \mu_3^p \\ ------------------------ \\ ------------------------ \\ \mu_c^1 = \mu_c^2 = \mu_c^3 = \quad -------- = \mu_c^p \end{array} \tag{6}$$

Since the number of variables in the system is $2 + (C-1)\,p$, and if f is the number of forces, the degree of freedom F would be given by

$$F = C - p + 2 + f \tag{7}$$

Considering only the gravitational field as a variable, it is obvious that in order that the degree of freedom may be zero for a one component system, we should have $p = 4$; i.e., there would exist an invariant point when four phases coexist in equilibrium. When the χ_j associated with the gravitational field is kept constant, the invariant point is called the triplepoint, and only three phases coexist in equilibrium at this temperature.

It is also obvious that

$$\left(\frac{\mathrm{d}P}{\mathrm{d}T}\right)_{\chi j} = \frac{\Delta S}{\Delta V} \tag{8}$$

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for a one-component system when the phases coexist in equilibrium. ΔS denotes the entropy change, and ΔV denotes the volume change during transformation from one phase to another. However, when the temperature, pressure, and the χ_j associated with the gravitational field is varying, Eq. (2) has to be used to obtain equilibrium relations. For constant T, we should have

$$\left(\frac{dP}{d\chi_j}\right)_T = -\frac{\Delta X_j}{\Delta V} \tag{9}$$

Similarly, for constant P we should have

$$\left(\frac{dT}{d\chi_j}\right)_p = \frac{\Delta X_j}{\Delta S} \tag{10}$$

The general equation would be as follows

$$\begin{aligned}\frac{dP}{dT} &= \frac{\Delta S}{\Delta V} - \frac{\Delta X_j}{\Delta V}\cdot\frac{d\chi_j}{dT}\\ &= \frac{\Delta H}{T\cdot\Delta V} - \frac{\Delta X_j}{\Delta V}\cdot\frac{d\chi_j}{dT}\end{aligned} \tag{11}$$

which would be the effective Clausius-Clapeyron relation for a one-component system. ΔH is the enthalpy change. During transformation from phase α to phase β, the electric dipole moment, magnetic dipole moment, and mz remain the same; therefore, for all practical purposes

$$\frac{dP}{dT} = \frac{\Delta H}{T\cdot\Delta V} \tag{12}$$

Thus, the dependence of boiling point or freezing point of a substance on vapor pressure would be the same in spite of the external fields.

Let us now examine the effect on chemical equilibrium in the external fields. Consider a term J defined as

$$J = G - X\chi \tag{13}$$

therefore

$$dJ = dG - x d\chi - \chi dx = -SdT + VdP - \chi dx \tag{14}$$

For an open system at equilibrium

$$dJ = -SdT + VdP - \chi dx + \sum_i \mu_i dn_i \tag{15}$$

where the chemical potential

$$\mu_i = \left(\frac{\partial J}{\partial n_i}\right)_{T,P,x,n_j} \tag{16}$$

Equation (16) can be integrated to yield

$$J = \sum_i \mu_i n_i \tag{17}$$

with

$$\mu_i = \mu_i^0 + RT\ln a_i, \quad K = \prod_i (a_i)_e^{\nu i} \tag{18}$$

where R is the gas constant, ν_i is the stoichiometric number, μ_i^0 depends on temperature and pressure, and a_i is the activity of component i. Now, with $dJ=0$, for a change at equilibrium at constant T, P, and X, we have

$$\begin{aligned}(\Delta J)_e = 0 = \sum_i \nu_i(\mu_i)_e &= \sum_i \nu_i\ [\mu_i^0 + RT\ln(a_i)_e]\\ &= \Delta J^0 + RT\ln K\end{aligned} \tag{19}$$

so that

$$\ln K = -\frac{\Delta J^0}{RT} = -\frac{\Delta G^0}{RT} + \frac{X\Delta\chi^0}{RT} = \ln K^0 + \frac{X\Delta\chi^0}{RT} \tag{20}$$

where K^0 is the equilibrium constant in the absence of external fields, and K is the corresponding value in the presence of an external field. Therefore, it follows that for a gravitational field g

$$\ln K = \ln K^0 + [g\Delta(mz)/RT]$$

for an electrical field E

$$\ln K = \ln K^0 + [E(\Delta\mu)/RT],$$

and for a magnetic field H

$$\ln K = \ln K^0 + [H\cdot(\Delta M)/RT],$$

where $\Delta\mu$ and ΔM are the respective differences in the electrical dipole moments, and magnetic dipole moments of products and reactants.

We report a typical calculation to estimate the influence of electrical field on the equilibrium constant. Consider the reaction

$$HI \rightleftharpoons H_2 + \tfrac{1}{2}I_2$$

We know that the electric dipole moment of HI is 0.38 Debye, whereas the dipole moment of H_2 and I_2 is zero. The difference in the dipole moment of products and reactants would therefore be $0.38\times10^{-18}\ \times\ 6.0225\times10^{23}$ esu cm/gm mole. Taking $E=10{,}000$ volt/cm, $T=730.6$K and $R=1.987$ cal/deg/gm mole, we have $E\cdot(\Delta\mu)/_{RT}$ equal to 1.256×10^{-4}. At this temperature, the value of the equilibrium constant in the absence of fields is 48.7.

From the foregoing calculations, it is clear that the effect of an electrical field on K^0 is negligibly small. However when K^0 is of very small magnitude, the influence may be significant provided $\Delta\mu$ is large.

Distribution of Components of a Mixture at Equilibrium in a Gravitational Field

Consider a binary mixture placed in a gravitational field. The change in chemical potential of component 2 in terms of mole fraction x_2 is given by

$$d\mu_2 = v_2 dP + M_2 g dz + \left(\frac{\partial\mu_2}{\partial x_2}\right)_{T,P,z} dx_2 \tag{21}$$

where M_2 is the molecular weight of component 2. In the gravitational field

$$dP = \rho g dz \tag{22}$$

where ρ is the density of the mixture. At equilibrium $d\mu_2 = 0$, therefore

$$(M_2 - v_2\rho)\cdot g dz = -(\partial\mu_2/\partial x_2)_{T,\rho,z} dx_2 \tag{23}$$

For an ideal gaseous mixture

$$\left(\frac{\partial\mu_2}{\partial x_2}\right)_{T,P,z} = \frac{RT}{x_2};\ v_2 = \frac{RT}{P};\ \rho = \frac{(x_1M_1 + x_2M_2)P}{RT} \tag{24}$$

Knowing that $x_1 + x_2 = 1$, we have

$$dx_1/dz = -[x_1x_2g(M_1 - M_2)/RT] \tag{25}$$

where M_1 is the molecular weight of component 1. In a zero gravity field, $dx_1/dz = 0$ which means x_1 = constant.

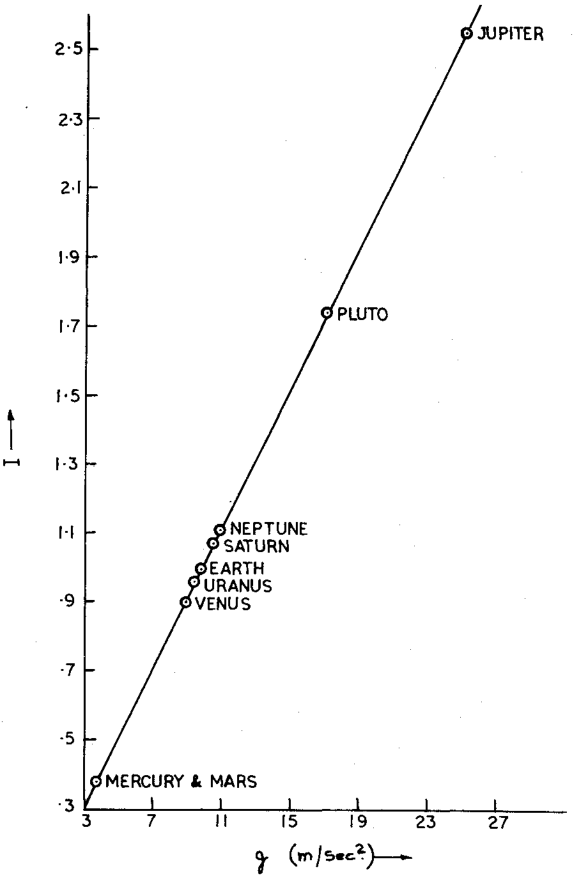

Fig. 1 Dependence of sedimentation current on gravity for different plantes. (ordinate in units of I for Earth).

Sedimentation Potential and Rate in Gravitational Fields

The irreversible thermodynamics of sedimentation phenomena have been discussed by de Grott,[4] and Rastogi and Misra.[5] When insoluble solid particles are allowed to fall under gravity, potential energy is converted into electrical energy and a sedimentation current flows. Moreover, in such a system, when an electric field is applied the particles move, giving rise to electrophoresis. The phenomenological relations can be written as

$$I=L_{11}\,E+L_{12}g \qquad (26)$$

$$J=L_{21}E+L_{22}g \qquad (27)$$

where E is the electric field and g is the gravitational field per unit mass. I is the electric current density and J is the material flux related to V_e, the electrophoretic velocity, in the following manner:

$$J=m(1-\rho_2/\rho_1)\cdot V_e \qquad (28)$$

where m is the mass of particles suspended between the two electrodes. ρ_1 and ρ_2 are the density of solid and liquid, respectively. When $E=0$

$$I=L_{12}g \qquad J=L_{22}g \qquad (29)$$

The value of I and J on the moon would be roughly one sixth of that on earth. Furthermore, under conditions of zero gravity

$$(I/E)_{g=0}=L_{11}\,(J/E)_{g=0}L_{21} \qquad (30)$$

In Fig. 1, the sedimentation current for a typical system is plotted against g for various planets in units of sedimentation current for earth.

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Quasi-Steady Gas Phase Assumption for a Burning Droplet

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Nomenclature

C $=C=c_F h_F^0+c_P h_P^0$
c_F $=w_F/w_O N_O$
c_P $=w_P N_P/w_O N_O$
C_p = total heat capacity at constant pressure, cal/g° K
D = diffusivity, cm^2/sec
h_i^0 = specific formation enthalpy for species i, cal/g
k_f = the Arrhenius term, cm^3/mole sec
N = stoichiometric number of moles
p = pressure, atm
P = nondimensional pressure
r = radial coordinate, cm
R = radius of the droplet, cm
$\tilde{R}$ = gas constant, cal/g° K
t = time, sec
T = temperature, ° K
u = velocity, cm/sec
w_i = molecular weight of species i, g/mole
y = nondimensional coordinate
Y_i = mass fraction for species i
z = nondimensional time
β = characteristic frequency, 1/sec
γ = the isentropic gas coefficient
θ = nondimensional temperature
λ = coefficient of heat conductivity, cal/cm° Ksec
ρ = density, g/cm^3
τ = characteristic time, sec

Subscripts

chem = chemical
d = droplet
F = fuel
g = gas
O $=O_2$
P = products
p = pressure
ref = reference
0 = initial conditions

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