

Chapter 6

Applications of Thermodynamics

6.1 INTRODUCTION

In the last chapter, a formulation of thermodynamics was presented that is specifically designed to be convenient for use in statistical mechanics. In this chapter, the subject of thermodynamics will be recast in its more customary form and a variety of practical applications of the theory will be exhibited. But first, the theory of chemical reaction equilibrium will be discussed using a mixture of thermodynamics and statistical mechanics.

6.2 CHEMICAL REACTIONS

The theory of chemical reaction equilibrium is one of the most successful applications of thermodynamics. As an example, we consider a dilute aqueous solution of three chemicals, A_2 , B , and AB , which participate in the reaction



The question we will consider is: At equilibrium, how are the concentrations of A_2 , B , and AB related? We will assume that the system is isolated and work in a rational system of units. The entropy is some function of N_{A_2} , N_B , N_{AB} , N_w , E , and V , where N_w is the number of molecules of water.

$$S^o = S^o(N_{A_2}, N_B, N_{AB}, N_w, E, V) \quad (6.2)$$

According to the reaction equation, if $2k$ molecules of AB are produced by the reaction, then $dN_{A_2} = -k$ and $dN_B = -2k$. The change in entropy would be

$$\begin{aligned} dS^o &= \alpha_{A_2} dN_{A_2} + \alpha_B dN_B + \alpha_{AB} dN_{AB} \\ &= k(2\alpha_{AB} - \alpha_{A_2} - 2\alpha_B) \end{aligned} \quad (6.3)$$

At equilibrium, S^o is a maximum with respect to all allowed changes, and thus dS^o should be zero for all very small values of k . The equilibrium condition is, therefore,

$$\alpha_{A_2} + 2\alpha_B = 2\alpha_{AB} \quad (6.4)$$

Comparing this with Eq. (6.1), the reaction equation, it is quite obvious how to write the equilibrium equation for any other chemical reaction. Notice that this is an exact result, that does not depend, as most of our future analysis will, upon any low density approximation.

For dilute solutions, Eq. (5.78) gives the affinities in terms of the densities.

$$\alpha_i = -\log n_i + f_i^o, \quad i = A_2, B, \text{ or } AB \quad (6.5)$$

The constant $f_{A_2}^o$ is a function of all intensive variables other than n_{A_2} . But, if all chemical concentrations are very small, then we can, in evaluating f_{A_2} , set n_B and n_{AB} equal to zero. Thus, $f_{A_2}^o$, f_B^o , and f_{AB}^o can be assumed to be functions of pressure and temperature only. Using this relation for α_i in Eq. (6.4) gives

$$\log\left(\frac{n_{AB}^2}{n_{A_2}n_B^2}\right) = 2f_{AB}^o - f_{A_2}^o - 2f_B^o \equiv \log K \quad (6.6)$$

where K is called the *equilibrium constant* for this reaction. The equilibrium condition can thus be written as

$$\frac{n_{AB}^2}{n_{A_2}n_B^2} = K \quad (6.7)$$

This relation is called the *law of mass action* for the reaction $A_2 + 2B \leftrightarrow 2AB$. In general, the reaction



will be in equilibrium when

$$\frac{n_R^r n_S^s \dots}{n_A^a n_B^b \dots} = K \quad (6.9)$$

where the integers, a, b, \dots, r, s, \dots are called the *stoichiometric coefficients* of the reaction and

$$\log K = rf_R^o + sf_S^o + \dots - af_A^o - bf_B^o - \dots \quad (6.10)$$

6.3 VAN'T HOFF'S LAW

For a reaction of the form $aA + bB \leftrightarrow rR$, the changes in N_A , N_B , and N_R caused by the reaction are related by $\Delta N_A/a = \Delta N_B/b = -\Delta N_R/r$. The quantity $k = \Delta N_R/r$ measures the number of individual forward reactions minus the number of back reactions that have taken place during any time interval. For a given k , the *heat of reaction*, W , is the amount of energy that would have to be removed from the system in order to maintain it at constant temperature divided by k . It is the energy given off by a single reaction. Therefore, at constant temperature and volume,

$$E(N_A, N_B, N_R) = E(N_A + \Delta N_A, N_B + \Delta N_B, N_R + \Delta N_R) + kW \quad (6.11)$$

This simply states that the initial energy of the system is equal to its final energy plus the energy removed from the system.

Using the facts that $\Delta N_A = -ak$, $\Delta N_B = -bk$, and $\Delta N_R = rk$, Eq. (6.11) can be written, for small k , as

$$a\left(\frac{\partial E}{\partial N_A}\right) + b\left(\frac{\partial E}{\partial N_B}\right) - r\left(\frac{\partial E}{\partial N_R}\right) = W \quad (6.12)$$

But

$$\left(\frac{\partial E}{\partial N_A}\right) = -\frac{\partial^2 \phi}{\partial N_A \partial \beta} = -\frac{\partial \alpha_A}{\partial \beta} \quad (6.13)$$

Thus

$$\frac{\partial}{\partial \beta}(r\alpha_R - a\alpha_A - b\alpha_B) = W \quad (6.14)$$

Since $\alpha_i = -\log n_i + f_i^o$ and $(\partial n_i / \partial \beta)_{N,V} = 0$, we see that the temperature dependence of the equilibrium constant is related to the heat of reaction by *Van't Hoff's law*.

$$\frac{\partial \log K}{\partial \beta} = W \quad (6.15)$$

This yields the reasonable result that, if energy is released in a reaction $A + B \rightarrow C + D$, then increasing the temperature will decrease the equilibrium constant, which will increase the proportion of particles in the high-energy forms A and B .

In practical units the equilibrium constant K is defined by Eq. (6.9), with all densities expressed in moles/m³. Then Van't Hoff's law has the form

$$R \frac{\partial \log K}{\partial (1/T)} = W \quad (6.16)$$

where W is given by Eq. (6.11) with all numbers expressed in moles. That is, W is the molar heat of the reaction.

6.4 IDEAL GAS REACTIONS

An excellent example of the powerful interaction of statistical mechanics and thermodynamics is provided by the study of reaction equilibrium among chemical components of a dilute gas. For an aqueous solution, the system is so complex and strongly interacting that there is little hope of actually carrying out the multidimensional integrations that define the thermodynamic potentials in statistical mechanics. However, for reactions among ideal gas constituents, it is often possible to make a purely theoretical calculation of the equilibrium constant. It is really quite remarkable that the properties of something as intrinsically complicated as a chemical reaction within a system containing a vast number of particles can be successfully predicted by purely mathematical analysis. We will describe two typical cases of ideal gas reaction calculations, although they use the concepts of statistical mechanics and therefore are somewhat out of place in this chapter.

The equilibrium condition in the presence of a chemical reaction



is that

$$a\alpha_A + b\alpha_B + \cdots = r\alpha_R + s\alpha_S + \cdots \quad (6.18)$$

Therefore, one can predict the equilibrium condition for reactions among ideal gas components if one can calculate the affinity of each component as a function of its density and the temperature. That can be done by considering the various gases separately.

For an ideal gas of N identical molecules, of any type, the partition function of the system, Z , can be written in terms of the partition function of a single molecule, z . [See Eq. (4.61).]

$$Z = \frac{z^N}{N!} \quad (6.19)$$

The partition function of a single molecule can be further separated into a translational and an internal factor.

$$z = z(\text{trans})z(\text{int}) \quad (6.20)$$

For molecular gases, the translational partition function may always be calculated using classical mechanics.

$$z(\text{trans}) = V/\lambda^3(\beta) \quad (6.21)$$

where λ is the thermal de Broglie wavelength. The internal partition function is given by a sum over the internal energy levels of the molecule or atom, taking into account the degeneracy g_n of each energy eigenvalue.

$$z(\text{int}) = \sum_n g_n e^{-\beta \varepsilon_n} \quad (6.22)$$

The canonical potential of the gas is the logarithm of Z .

$$\begin{aligned} \phi &= \log(z^N/N!) \\ &= \log[z(\text{trans})z(\text{int})/N!] \\ &= N \left[\log(V/N) + 1 + \log(z(\text{int})/\lambda^3) \right] \end{aligned} \quad (6.23)$$

According to this equation, the affinity of an ideal gas, at any concentration, has the same form as the affinity of a dilute solution.

$$\alpha = \frac{\partial \phi}{\partial N} = -\log n + \log [z(\text{int})/\lambda^3] \quad (6.24)$$

Equation (6.10), for the equilibrium constant of a chemical reaction within a dilute solution, is valid at all concentrations for reactions among ideal gas constituents, since it was derived using only the above form for the affinity. The term f_i^o in the formula

$$\alpha_i = -\log n_i + f_i^o \quad (6.25)$$

is called the *chemical constant* of the i th component of the gas (or dilute solution). From Eq. (6.24), it is clear that a theoretical calculation of the chemical constant for any ideal gas component requires only a knowledge of the internal partition function for that component. That is,

$$f_i^o(T) = \log [z_i(\text{int})/\lambda_i^3] \quad (6.26)$$

One can see that, for an ideal gas (but not for a dilute solution), the chemical constant is a function of the temperature alone. It does not depend on the pressure.

6.5 MOLECULAR DISSOCIATION

At any fixed temperature and density, a gas of diatomic molecules reaches dissociation–recombination equilibrium with its atomic constituents. As the temperature is increased at constant density or the density is decreased at constant temperature, the equilibrium shifts in the direction of dissociation. If the dissociation of the diatomic molecule is taken to be the forward reaction, then the chemical reaction equation is of the form



For such a reaction, according to Eqs. (6.10) and (6.26), the equilibrium constant is given by

$$\log K = \log [z_A(\text{int})/\lambda_A^3] + \log [z_B(\text{int})/\lambda_B^3] - \log [z_{AB}(\text{int})/\lambda_{AB}^3] \quad (6.28)$$

From the fact that $m_{AB} = m_A + m_B$ and the definition of the thermal de Broglie wavelength, one can easily show that $\lambda_A \lambda_B / \lambda_{AB} = \lambda_\mu$, where μ is the reduced mass, $\mu = m_A m_B / (m_A + m_B)$. Thus, Eq. (6.28) can be written as

$$K = \frac{z_A(\text{int})z_B(\text{int})}{z_{AB}(\text{int})\lambda_\mu^3} \quad (6.29)$$

In evaluating the equilibrium constant, the following approximations will be made:

1. The calculation will initially be restricted to heteronuclear diatomic molecules, and the necessary modification for homonuclear molecules will be given at the end. (See Section 4.11 for the definition of homonuclear and heteronuclear molecules.)
2. Electronic excited states will be ignored in the molecule. Since electronic excitation levels are typically of the order of electron volts and one eV corresponds to a temperature of about 10,000 K, this is generally a good approximation at the dissociation temperatures of diatomic molecules. If the temperature is high enough to require the consideration of electronic excited states, then it is usually high enough to require the consideration of ionization phenomena also.
3. Hyperfine structure of the atomic ground states will be neglected. Hyperfine structure causes a splitting of otherwise degenerate energy levels due to the orientation of the nuclear spin \mathbf{S}_{nuc} relative to the total electronic spin, \mathbf{S} , and the total orbital angular momentum \mathbf{L} . The hyperfine levels are very closely spaced, and thus, at any temperature at which a molecule is likely to dissociate, they can be considered as degenerate.
4. The molecular rotational levels will be treated classically. This is an excellent approximation at all temperatures relevant to molecular dissociation.
5. The vibrational levels of the molecule will be approximated by a pure harmonic oscillator spectrum. Because of the rapid convergence of the partition function sum over vibrational energy levels, this is generally a good approximation.

If the zero-energy state is taken to be the state in which all atoms are infinitely separated and at rest, then the ground-state energy values of the isolated atoms are zero and the atomic partition function is given by

$$z_A(\text{int}) = g_o + g_1 e^{-\beta\varepsilon_1} + \dots \quad (6.30)$$

where ε_n and g_n are the energy and degeneracy of the n th level of atom A . Only those levels need to be taken into account for which ε_n is not much larger than kT . Often this includes only the ground state (see Table 6.2). A similar equation holds for $z_B(\text{int})$.

The internal energy levels of the AB molecule can be approximated by the formula

$$\varepsilon = -\varepsilon_B + \frac{l(l+1)\hbar^2}{2I_{AB}} + n\hbar\omega \quad (6.31)$$

where ε_B is the molecular binding energy (the absolute value of the difference between the ground-state energy of a molecule and the ground-state energies of its constituent atoms), I_{AB} is the moment of inertia of the molecule, $l(l+1)\hbar^2/2I_{AB}$ is the $(2l+1)$ -degenerate rotational energy state, and $n\hbar\omega$ is the vibrational excitation energy (the zero-point vibrational energy is included in $-\varepsilon_B$). Since the energy levels are a sum of three independent terms, the internal partition function splits into factors.

$$z_{AB}(\text{int}) = e^{\beta\varepsilon_B} z_{AB}(\text{rot}) z_{AB}(\text{vib}) \quad (6.32)$$

Using the classical approximation, $z_{AB}(\text{rot})$ was calculated in Section 4.11.

$$z_{AB}(\text{rot}) = 2I_{AB}/\beta\hbar^2 \quad (6.33)$$

The vibrational partition function is easily calculated by using the sum for a geometrical series.

$$z_{AB}(\text{vib}) = \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} = \frac{1}{1 - e^{-\beta\hbar\omega}} \quad (6.34)$$

Combining the two factors gives

$$z_{AB}(\text{int}) = \frac{(2I_{AB}/\beta\hbar^2)e^{\beta\varepsilon_B}}{1 - e^{-\beta\hbar\omega}} \quad (6.35)$$

For homonuclear molecules whose nuclei have zero spin, the internal wave function of the molecule must have the symmetry property,

$$\psi(\mathbf{R}_1, \mathbf{R}_2) = \pm\psi(\mathbf{R}_2, \mathbf{R}_1) \quad (6.36)$$

where the $+$ sign holds if the nuclei (which are always identical for a homonuclear molecule) are Bose–Einstein particles and the $-$ sign holds if they are Fermi–Dirac particles. We will not consider the case of homonuclear molecules with nonzero spin because then the wave function also contains spin variables and the situation is considerably more complicated. It can be shown that the symmetry of a wave function depends only upon the value of ℓ , the angular momentum quantum number. If ℓ is even, then the wave function is unchanged when $\mathbf{R}_1 \rightleftharpoons \mathbf{R}_2$ and if ℓ is odd the wave function changes sign. Thus, for boson nuclei one must sum only over even values of ℓ in calculating $z_{A_2}(\text{rot})$ and for fermion nuclei one must sum only over odd values. In both cases, when the classical approximation is valid the net effect is simply to reduce $z_{A_2}(\text{rot})$ by a factor of $\frac{1}{2}$. Thus, for homonuclear molecules,

$$z_{A_2}(\text{int}) = \frac{(I/\beta\hbar^2)e^{\beta\varepsilon_B}}{1 - e^{-\beta\hbar\omega}} \quad (6.37)$$

The values of the molecular parameters ε_B , ω , and I for a selection of heteronuclear and homonuclear diatomic molecules are given in Table 6.1.

	E_B	$\hbar\omega$	$\hbar^2/2I$
O ₂	6.0×10^4	2250	2.07
S ₂	5.1×10^4	702	0.42
Ca ₂	1.4×10^3	65	0.066
Mg ₂	3.6×10^3	51	0.13
CaO	4.7×10^4	1056	0.50
CaS	3.7×10^4	824	0.26
MgO	4.8×10^4	902	0.70
MgS	2.8×10^4	761	0.39

TABLE 6.1 Molecular parameters of O, S, Ca, and Mg diatomics, which are composed of atoms with zero nuclear spin; all energies are in Kelvins.

atom	levels
H	$^2S_{1/2}(0)$, $^2P_{1/2}(118349)$, $^2S_{1/2}(118349)$, $^2P_{3/2}(118349)$
D	$^2S_{1/2}(0)$, $^2P_{1/2}(118381)$, $^2S_{1/2}(118381)$, $^2P_{3/2}(118382)$
He	$^1S_0(0)$, $^2S_1(229982)$, $^1S_0(239221)$
Li	$^2S_{1/2}(0)$, $^2P_{1/2}(21443)$, $^2P_{3/2}(21443)$
Be	$^1S_0(0)$, $^3P_0(31622)$, $^3P_1(31623)$, $^3P_2(31626)$
B	$^2P_{1/2}(0)$, $^2P_{3/2}(23.02)$, $^4P_{1/2}(41443)$, $^4P_{3/2}(41450)$, $^4P_{5/2}(41459)$
C	$^3P_0(0)$, $^3P_1(23.60)$, $^3P_2(62.59)$, $^1D_2(14666)$
N	$^4S_{3/2}(0)$, $^2D_{5/2}(27657)$, $^2D_{3/2}(27668)$
O	$^3P_2(0)$, $^3P_1(228.04)$, $^3P_0(325.87)$, $^1D_2(22830)$
F	$^3P_{3/2}(0)$, $^3P_{1/2}(581.25)$, $^4P_{5/2}(147337)$
Ne	$^1S_0(0)$, $^X X_2(192854)$
Na	$^2S_{1/2}(0)$, $^2P_{1/2}(24395)$, $^2P_{3/2}(24420)$
Mg	$^1S_0(0)$, $^3P_0(31436)$, $^3P_1(31465)$, $^3P_2(31524)$
Al	$^2P_{1/2}(0)$, $^2P_{3/2}(161.20)$, $^2S_{1/2}(36469)$
Si	$^3P_0(0)$, $^3P_1(111.00)$, $^3P_2(321.27)$, $^1D_2(9063)$
P	$^4S_{3/2}(0)$, $^2D_{3/2}(16347)$, $^2D_{5/2}(16368)$
S	$^3P_2(0)$, $^3P_1(571.0)$, $^3P_0(825.3)$, $^1D_2(13292)$
Cl	$^2P_{3/2}(0)$, $^2P_{1/2}(1268)$, $^4P_{5/2}(103523)$
A	$^1S_0(0)$, $^X X_2(134010)$
K	$^2S_{1/2}(0)$, $^2P_{1/2}(18682)$, $^2P_{3/2}(18765)$
Ca	$^1S_0(0)$, $^3P_0(21808)$, $^3P_1(21883)$, $^3P_2(22036)$

TABLE 6.2 A table of the low-lying quantum states of the first 20 elements (including deuterium). The states are denoted with the usual LS-coupling symbol, which gives $^{2S+1}L_J$, where S is the total spin, L is the total orbital angular momentum (in spectroscopist's peculiar notation), and J is the combined angular momentum of the state. The symbol $^X X_J$ means that LS-coupling does not work for this state. The number in parentheses is the energy of the state in Kelvins. The degeneracy of each level is $2J + 1$.

6.6 IONIZATION—THE SAHA EQUATION

At standard temperature and pressure, hydrogen is a gas of diatomic molecules. If the pressure is kept constant, but the temperature is increased, then, at about 4000 K, the diatomic molecules dissociate and, by 6000 K, the gas is composed almost entirely of individual atoms. If the temperature is increased further, at about 10,000 K, the atoms begin to decompose into their constituent electrons and protons. That ionization process can be analyzed by the same formulas as were used for the dissociation of a diatomic molecule. The chemical reaction is (p and e stand for proton and electron)



Both the proton and the electron are spin- $\frac{1}{2}$ particles and therefore have two possible spin states. In the absence of a magnetic field, the two spin states have equal energy, which we can take to be zero. Thus

$$z_p = 2 \quad \text{and} \quad z_e = 2 \quad (6.39)$$

The internal partition function of the hydrogen atom is

$$z_H = \sum_n g_n e^{-\beta \varepsilon_n} \quad (6.40)$$

where the n th hydrogenic energy eigenvalue is $\varepsilon_n = -\varepsilon_o/n^2$ with $\varepsilon_o = 2.18 \times 10^{-18}$ J. The degeneracy of the n th level is $g_n = 4n^2$, where the factor of 4 comes from the two possible spin states of the proton and electron in the hydrogen atom. We will show that, at the temperatures at which ionization occurs, it is a good approximation to neglect all states in the sum except the ground state. Then

$$z_H = 4e^{\beta \varepsilon_o} \quad (6.41)$$

Because of the large ratio of the proton mass to the electron mass, the reduced mass is negligibly different from the electron mass. Therefore, using Eq. (6.29), one gets an equation first derived by Saha in 1921.

$$\frac{n_p n_e}{n_H} = K(T) = \frac{z_p z_e}{z_H \lambda_e^3} = \frac{e^{-\beta \varepsilon_o}}{\lambda_e^3} \quad (6.42)$$

We must still show that the neglect of excited atomic states is justified. At 20,000 K, a temperature at which the gas is almost totally ionized, the ratio of the probability of finding an atom in the first excited state to that of finding it in the ground state is

$$\frac{\mathbf{P}[n = 2]}{\mathbf{P}[n = 1]} = 4e^{-(\varepsilon_2 - \varepsilon_1)/kT} \approx 0.01 \quad (6.43)$$

The factor of four in this formula is due to the fourfold degeneracy of the $n = 2$ state.

6.7 THE ENERGY REPRESENTATION

Among the variables N , E , V , and S , the entropy stands out as being of a fundamentally different character. N , E , and V are perfectly well defined for a system of three particles in a hard-walled box. They are mechanical or geometrical variables that have meanings outside of the domain of statistical mechanics or thermodynamics. In contrast, S is a statistical or probabilistic concept that has no obvious extension to small deterministic systems. Therefore, it was natural to base thermodynamics on a study of the function $S(N, E, V)$, which gives the new variable in terms of the old, familiar variables. However, for historical reasons, this is not the usual approach to thermodynamics. Thermodynamic information is usually presented in what is called the energy representation, in which E is given as a function of S , V , and N .

$$E = E(S, V, N) \quad (6.44)$$

(According to the definition of a representation that was given in Section 5.22, the energy representation should more properly be called the (S, V, N) representation.) The functions $S(N, E, V)$ and $E(S, V, N)$ contain the same physical information expressed in different forms. Given the values of three of the variables N , E , V , S , either function would allow one to determine the value of the fourth.

The partial derivatives of the function $E(S, V, N)$ can be expressed in terms of measurable properties of the system in the following way. We first write Eq. (5.39) for dS in the form

$$dS = \alpha dN + \frac{dE + p dV}{T} \quad (6.45)$$

Solving this for dE gives

$$dE = T dS - p dV - T\alpha dN \quad (6.46)$$

But it is a mathematical identity that

$$dE(S, V, N) = \left(\frac{\partial E}{\partial S}\right)_{VN} dS + \left(\frac{\partial E}{\partial V}\right)_{SN} dV + \left(\frac{\partial E}{\partial N}\right)_{SV} dN \quad (6.47)$$

which shows immediately that

$$\left(\frac{\partial E}{\partial S}\right)_{NV} = T, \quad \left(\frac{\partial E}{\partial V}\right)_{SN} = -p \quad (6.48)$$

and

$$\left(\frac{\partial E}{\partial N}\right)_{SV} = -T\alpha \equiv \mu \quad (6.49)$$

where μ is called the *chemical potential* of the substance. In terms of the chemical potential, dE can be expressed as

$$dE = T dS - p dV + \mu dN \quad (6.50)$$

6.8 F , H , AND G IN THE ENERGY REPRESENTATION

S , V , and N are all extensive variables. By means of Legendre transformations, any one or two of them may be replaced by corresponding intensive variables. In considering such transformations we will restrict ourselves to the case of a simple substance and assume that N is fixed and equal to one mole. Therefore, the function $E(S, V)$ is the molar energy as a function of the molar entropy and the molar volume. Then, with $dN = 0$,

$$dE(S, V) = T dS - p dV \quad (6.51)$$

In order to eliminate S in favor of T , we define a function, called the *Helmholtz free energy*, by

$$F(T, V) \equiv E - TS \quad (6.52)$$

Then Eq. (6.51) for dE gives

$$dF(T, V) = -S dT - p dV \quad (6.53)$$

To transform from (S, V) to (S, p) we define the *enthalpy* function

$$H(S, p) \equiv E + pV \quad (6.54)$$

which satisfies the differential relation

$$dH(S, p) = T dS + V dp \quad (6.55)$$

and lastly, to transform from (S, V) to (T, p) we define the *Gibbs free energy*

$$G(T, p) \equiv E - TS + pV \quad (6.56)$$

which satisfies the differential relation

$$dG(T, p) = -S dT + V dp \quad (6.57)$$

6.9 THE MAXWELL RELATIONS

The equation $dE = T dS - p dV$ implies that $(\partial E/\partial S)_V = T$ and $(\partial E/\partial V)_S = -p$. But, these relations allow the mixed partial derivative to be written in two equivalent forms, $\partial^2 E/\partial S \partial V = \partial^2 E/\partial V \partial S$, giving the *Maxwell relation*

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad (6.58)$$

In the same way, the facts that $(\partial F/\partial T)_V = -S$ and $(\partial F/\partial V)_T = -p$ lead to the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad (6.59)$$

and corresponding relations, involving H and G , give two further Maxwell relations

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \quad (6.60)$$

and

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad (6.61)$$

6.10 THE USE OF THERMODYNAMIC TABLES

In making any practical use of thermodynamics one must refer to standard compilations of physical properties, such as the *Handbook of Chemistry and Physics*, to obtain the essential thermodynamic functions for any particular substance. In most cases, the physical properties are tabulated as functions of temperature and pressure, for the simple reason that, experimentally, those are usually the variables that are easiest to accurately control. Not every conceivable physical property is tabulated. For a given substance, one can typically find the molar entropy and the molar volume as functions of p and T . Also commonly available are the constant pressure molar heat capacity,

$$C_p = \left(\frac{\partial Q}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p \quad (6.62)$$

the temperature coefficient of expansion,

$$\beta_p = V^{-1} \left(\frac{\partial V}{\partial T}\right)_p \quad (6.63)$$

and the isothermal compressibility,

$$\kappa_T = -V^{-1} \left(\frac{\partial V}{\partial p}\right)_T \quad (6.64)$$

The five quantities S , V , C_p , β_p , and κ_T are equivalent to the set of first and second derivatives of the molar Gibbs free energy. In particular, $S = -(\partial G/\partial T)$, $V = (\partial G/\partial p)$, $C_p = -T(\partial^2 G/\partial T^2)$, $\beta_p = (\partial^2 G/\partial T \partial p)/V$, and $\kappa_T = -(\partial^2 G/\partial p^2)/V$, as can be verified from Eq. (6.57). Therefore, in terms of these five quantities, it should be possible to express any quantity that involves first and second derivatives of any thermodynamic potentials as a function of p and T . This is enough to evaluate almost any quantity that is likely to appear in a normal thermodynamic analysis.

6.11 TRANSFORMATION OF VARIABLES

The thermodynamic space of a simple substance is three dimensional. However, when we fix the particle number at one mole, as we have, the set of possible equilibrium states becomes two dimensional. That means

that fixing the values of any two independent thermodynamic parameters is enough to define the state of the substance and hence to determine the values of all other thermodynamic variables. It is not uncommon, in practical calculations, for very strange combinations of variables to appear naturally. For example, in certain processes one can show that the enthalpy H remains constant (see Problem 6.12). Determining how the temperature varies with the pressure in such a process requires that one calculate the partial derivative $(\partial T/\partial p)_H$, which is just the partial derivative of the function $T(p, H)$. It is therefore important that one be able to convert almost any conceivable combination of partial derivatives of thermodynamic variables to some standard form in which they may be evaluated. In this section a systematic procedure will be given to convert any expression involving partial derivatives of the thermodynamic quantities p, T, S, V, E, F, H, G , and μ into an expression involving only p and T and the five "handbook variables," S, V, C_p, β_p , and κ_T . This is equivalent to evaluating an arbitrary partial derivative in the p - T representation. The procedure makes use of the three types of information listed here.

1. Differential relations

$$\begin{aligned}dE &= T dS - p dV \\dF &= -S dT - p dV \\dH &= T dS + V dp \\dG &= -S dT + V dp\end{aligned}\tag{6.65}$$

Of these, only the first needs to be memorized; the others are obtained by Legendre transformations, which give predictable sign changes in the terms.

2. Definitions of C_p, β_p , and κ_T

$$\begin{aligned}C_p &= T \left(\frac{\partial S}{\partial T} \right)_p \\ \beta_p &= V^{-1} \left(\frac{\partial V}{\partial T} \right)_p = -V^{-1} \left(\frac{\partial S}{\partial p} \right)_T \\ \kappa_T &= -V^{-1} \left(\frac{\partial V}{\partial p} \right)_T\end{aligned}\tag{6.66}$$

In the formula for β_p one of the Maxwell relations has been used.

3. Partial derivative identities Given any set of variables x, y, z , and w that have the property that the values of any two of the variables determine those of the others, then

$$\left(\frac{\partial x}{\partial y} \right)_z = \frac{1}{\left(\frac{\partial y}{\partial x} \right)_z}\tag{6.67}$$

$$\left(\frac{\partial x}{\partial y} \right)_z = - \frac{\left(\frac{\partial z}{\partial y} \right)_x}{\left(\frac{\partial z}{\partial x} \right)_y}\tag{6.68}$$

and

$$\left(\frac{\partial x}{\partial y} \right)_z = \frac{\left(\frac{\partial x}{\partial w} \right)_z}{\left(\frac{\partial y}{\partial w} \right)_z}\tag{6.69}$$

The first identity follows from the fact that, once the value of z has been fixed, x becomes a function of y and vice versa. But, for functions of one variable, $dx/dy = (dy/dx)^{-1}$.

The second identity can be derived from the differential relation

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy\tag{6.70}$$

If we set dz equal to zero, then the ratio of dx to dy is just $(\partial x/\partial y)_z$. This gives

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x = 0 \quad (6.71)$$

which is equivalent to the desired identity.

The third identity can be derived by considering two neighboring points that have the same values of z . The changes in x , y , and w are related by

$$dx = \left(\frac{\partial x}{\partial w}\right)_z dw, \quad dy = \left(\frac{\partial y}{\partial w}\right)_z dw, \quad \text{and} \quad \left(\frac{\partial x}{\partial y}\right)_z = \frac{dx}{dy} \quad (6.72)$$

from which the identity follows immediately.

Our task is now to convert any partial derivative expression, such as $(\partial\mu/\partial p)_H$ or $(\partial S/\partial V)_p$, into an expression involving p , T , S , V , and derivatives of the form

$$\left(\frac{\partial(S \text{ or } V)}{\partial(p \text{ or } T)}\right)_{(T \text{ or } p)} \quad (6.73)$$

which can all be written in terms of handbook quantities. We will do this in two stages. Calling p , T , S , and V the *good* variables and E , F , H , G , and μ the *bad* variables, we will first eliminate all bad variables in favor of good variables. Then we will transform any resulting partial derivatives, which will only involve good variables, to the specific form shown in Eq. (6.73).

In eliminating the bad variables, the chemical potential μ is a special case. It is eliminated by using the fact that (see Problem 6.10) the chemical potential of any substance is always equal to the molar Gibbs free energy. Thus μ is simply replaced by G . We now introduce the convention that a and b denote good variables, α denotes a bad variable, and x , y , and z may be either good or bad.

To transform a term of the form $(\partial\alpha/\partial x)_y$, one uses the corresponding differential relation. For example, the relation, $dH = T dS + V dp$ gives

$$\left(\frac{\partial H}{\partial x}\right)_y = T \left(\frac{\partial S}{\partial x}\right)_y + V \left(\frac{\partial p}{\partial x}\right)_y \quad (6.74)$$

Notice that this will never introduce any new bad variables.

To eliminate a term of the form $(\partial a/\partial\alpha)_x$, one uses the first partial derivative identity.

$$\left(\frac{\partial a}{\partial\alpha}\right)_x = \frac{1}{\left(\frac{\partial\alpha}{\partial a}\right)_x} \quad (6.75)$$

followed by the appropriate differential relation to eliminate α . These two procedures will eliminate bad variables as either numerators or denominators in partial derivative expressions. The only remaining possibilities are expressions of the form $(\partial a/\partial b)_\alpha$. These are converted by the second partial derivative identity.

$$\left(\frac{\partial a}{\partial b}\right)_\alpha = -\frac{\left(\frac{\partial\alpha}{\partial b}\right)_a}{\left(\frac{\partial\alpha}{\partial a}\right)_b} \quad (6.76)$$

followed by the use of a differential relation to eliminate α entirely.

With these procedures we can reduce any partial derivative to ones containing only p , T , S , and V . If these are not in the desired form, shown in Eq. (6.73), then they can be converted to that form as follows.

For an expression of the form

$$\left(\frac{\partial(p \text{ or } T)}{\partial(S \text{ or } V)}\right)_{(T \text{ or } p)} \quad (6.77)$$

we use the first partial derivative identity.

For an expression of the form

$$\left(\frac{\partial(p \text{ or } T)}{\partial(T \text{ or } p)}\right)_{(S \text{ or } V)} \quad (6.78)$$

we use the second partial derivative identity. The remaining possibilities are expressions of the form

$$\left(\frac{\partial(S \text{ or } V)}{\partial(p \text{ or } T)}\right)_{(V \text{ or } S)} \quad \text{or} \quad \left(\frac{\partial(S \text{ or } V)}{\partial(V \text{ or } S)}\right)_{(p \text{ or } T)} \quad (6.79)$$

The first of these is converted to the standard form by the procedure illustrated.

$$\left(\frac{\partial S}{\partial p}\right)_V \equiv \frac{\partial S(p, V)}{\partial p} = \frac{\partial S(p, T(p, V))}{\partial p} = \left(\frac{\partial S}{\partial p}\right)_T + \left(\frac{\partial S}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_V \quad (6.80)$$

which reduces it to the immediately previous case. The second case requires the third partial derivative identity.

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\left(\frac{\partial S}{\partial p}\right)_T}{\left(\frac{\partial V}{\partial p}\right)_T} \quad (6.81)$$

6.12 A FORMULA FOR $C_p - C_v$

An important example of the foregoing type of analysis is the following derivation of a formula for the difference between the constant pressure and constant volume molar specific heats. The definition of C_v is

$$C_v = \left(\frac{\partial Q}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V \quad (6.82)$$

But

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_V &= \frac{\partial S(T, V)}{\partial T} = \frac{\partial S(T, p(V, T))}{\partial T} \\ &= \left(\frac{\partial S}{\partial T}\right)_p + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V \end{aligned} \quad (6.83)$$

Using the facts that

$$T \left(\frac{\partial S}{\partial T}\right)_p = C_p, \quad (6.84)$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -V\beta_p, \quad (6.85)$$

and

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\beta_p}{\kappa_T} \quad (6.86)$$

we obtain the desired formula for $C_p - C_v$.

$$C_p - C_v = TV\beta_p^2/\kappa_T \quad (6.87)$$

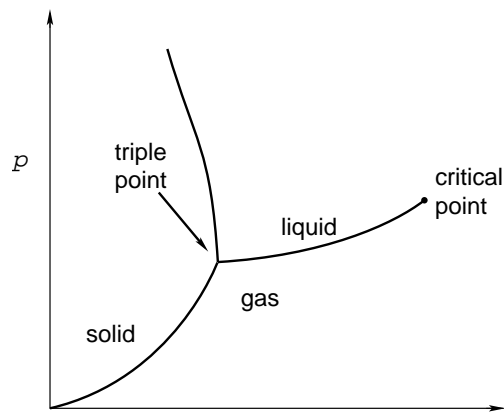


Fig. 6.1 A typical phase diagram. The gas–liquid transition line extends from the triple point to the critical point, at which the properties of the gas and the liquid become indistinguishable and thus the phase transition disappears.

6.13 THE CLAUSIUS–CLAPEYRON EQUATION

The phase diagram of an imaginary substance is shown in Fig. 6.1. At most combinations of temperature and pressure, the equilibrium state of the substance is a single uniform phase: solid, liquid, or gas. These regions of single-phase states are separated by two-phase *coexistence curves*. It is impossible to compute the phase diagram of any substance using the laws of thermodynamics. The equilibrium phase at given p and T depends upon the details of the microscopic structure of the substance. However, the laws of thermodynamics do provide an important relation between the slope of any coexistence curve and the changes in S and V associated with the corresponding phase transition. In deriving this relation, called the Clausius–Clapeyron equation, we will consider the gas–liquid condensation curve. At any point (p, T) on that curve, a two-phase system composed of gas and liquid could remain at equilibrium within a single container. Besides the obvious requirements that the temperatures and pressures in the two phases be equal, the third condition for equilibrium between two phases is that the affinities of gas and liquid be equal. Since the temperatures are equal, this equality of the affinities implies the equality of the chemical potentials. Thus, all along the condensation curve,

$$\mu_L(p, T) = \mu_G(p, T) \quad (6.88)$$

But, as noted earlier, the chemical potential of any substance is equal to its molar Gibbs free energy, $G(p, T)$. If we consider two neighboring points on the condensation curve, then the condition that $d\mu_L = d\mu_G$, and Eq. (6.65), which states that $d\mu = -S dT + V dp$, where S and V are the molar entropy and volume, implies that

$$-S_L dT + V_L dp = -S_G dT + V_G dp \quad (6.89)$$

Solving for dp/dT gives the slope of the condensation curve in the p - T plane.

$$\frac{dp}{dT} = \frac{S_G - S_L}{V_G - V_L} \quad (6.90)$$

In converting one mole of liquid to one mole of gas at the same temperature, an amount of heat energy, called the *latent heat of evaporation* L , must be added to the substance. Since the process is carried out at fixed temperature, the equation $dS = dQ/T$ implies that $S_G - S_L = L/T$. Thus the Clausius–Clapeyron equation may be expressed in the alternative form

$$\frac{dp}{dT} = \frac{L}{T(V_G - V_L)} \quad (6.91)$$

A useful set of approximations for many substances is: (1) to consider L as a constant, (2) to ignore V_L in comparison with V_G , and (3) to use the ideal gas law for V_G , namely $pV_G = RT$, where R is the molar gas constant. Then, we obtain the equation

$$\frac{dp}{dT} = \frac{Lp}{RT^2} \quad (6.92)$$

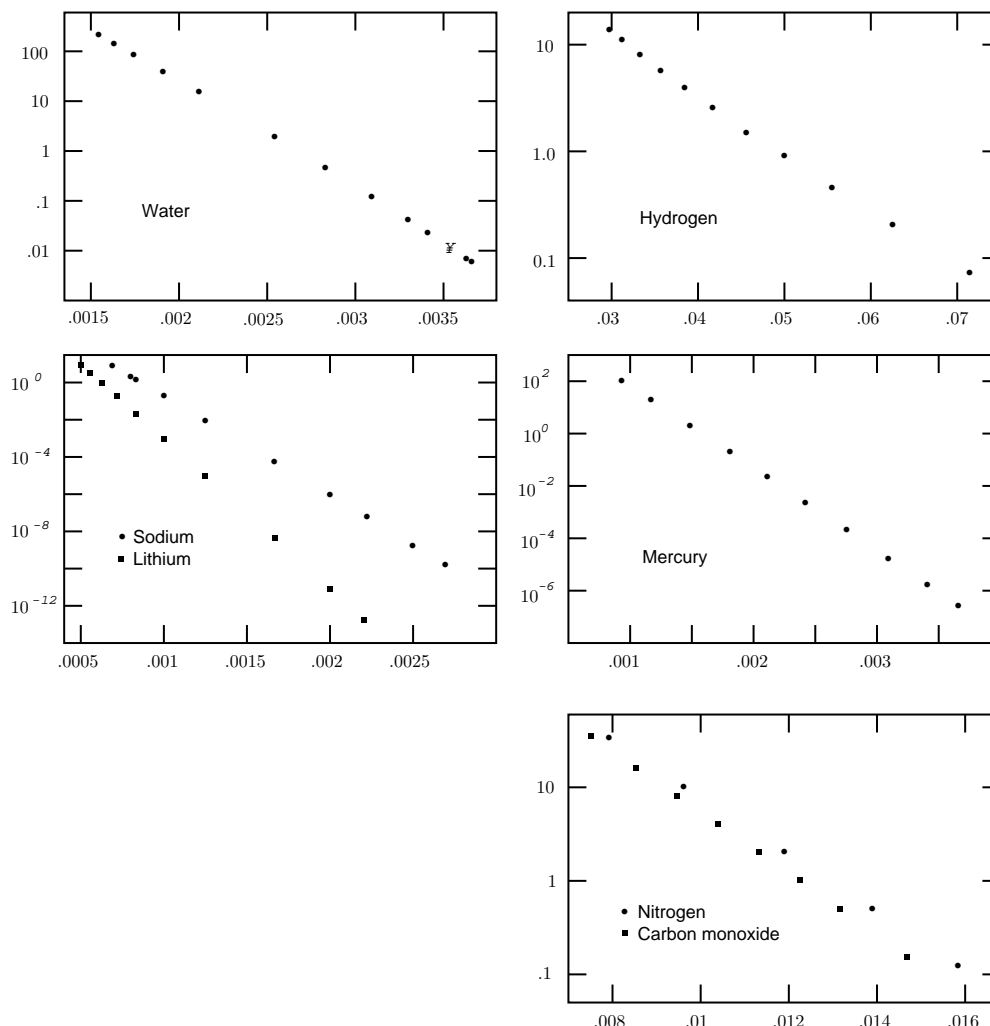


Fig. 6.2 The condensation curves for a variety of different substances. The vertical axis shows the *vapor pressure* (in bars), on a log scale, in a two-phase equilibrium state. The horizontal axis gives $1/T$, the inverse temperature. According to Eq. (6.94), the points should lie on a line whose slope gives the latent heat of the transition. Notice that the pressure ranges over which the linear approximation is accurate are typically very large.

which can be easily integrated by first rewriting it in the form

$$d(\log p) = \frac{dp}{p} = \frac{L}{R} \frac{dT}{T^2} = -\frac{L}{R} d\left(\frac{1}{T}\right) \quad (6.93)$$

yielding

$$\log p(T) = \text{const.} - \frac{L}{RT} \quad (6.94)$$

Figure 6.2 compares this approximate result with the experimental condensation curves for a number of substances.

6.14 THE CLASSIFICATION OF PHASE TRANSITIONS

The entropy function has a different form for each bulk phase of a substance. All other thermodynamic potentials, such as the canonical potential or the Helmholtz free energy, are defined in terms of the entropy, and therefore the same statement can be made for them; they have different forms for each phase of a

substance. In fact, this can be used as the defining characteristic of a phase transition. For example, if we look at one mole of a simple substance, in the p - T representation, then the natural thermodynamic potential is the Gibbs free energy, $G(p, T)$. In Fig. 6.2, on any phase transition line, the values of $G(p, T)$ of the two adjacent phases must be equal. That is, $G(p, T)$ must be a continuous function over the whole plane. Away from the phase transition lines, the derivatives of G give the molar entropy and the molar volume, and they must therefore also be continuous. If we run along any phase transition line, then the rates of change of G on the two sides of the line must be equal. That is, the directional derivative of G in the direction along a phase transition line must also be continuous. This is exactly the condition that is expressed in the Clausius–Clapeyron equation. However, the derivatives of G in the direction normal to the line do not have to be continuous. A long time ago, it was suggested by P. Ehrenfest that phase transitions be classified according to the behavior of the normal derivatives of G as we cross the phase transition line. If the normal derivative of G is discontinuous across the phase transition line then the phase transition was called a *first-order transition*. If the first derivative of G is continuous, but the second derivative has a discontinuity at the phase transition line, then the phase transition was called a *second-order transition*, and so on for third and higher derivatives. Unfortunately, nature has not cooperated with the Ehrenfest scheme. Except for the important case of first-order phase transitions, most of the phase transitions that actually occur do not fit into it.

It is now common practice to separate phase transitions into two classes. First-order phase transitions are those in which the microscopic structure of a substance undergoes a discontinuous change across the phase transition line. This class happens to agree with the old Ehrenfest class of first-order transitions. Second-order transitions are all those in which all microscopic structural properties of the substance vary continuously (but perhaps not differentially) across the phase transition line. The most important subset of second-order phase transitions are the *critical-point* transitions. A critical-point transition separates two phases in which there are different numbers of thermodynamic variables. A ferromagnetic solid gives an excellent example. For a ferromagnet, above a certain temperature, called the *Curie temperature*, the pressure and temperature uniquely define all properties of the equilibrium state. If T is less than the Curie temperature, then the substance spontaneously magnetizes itself. The direction of the magnetization cannot be predicted from the values of p and T and therefore must be introduced as a new independent thermodynamic variable. However, the amount of the magnetization goes continuously to zero as T approaches the Curie temperature—thus the microscopic properties vary continuously across the transition and so it is a second-order phase transition. A more detailed discussion of this topic will be given in Chapter 9.

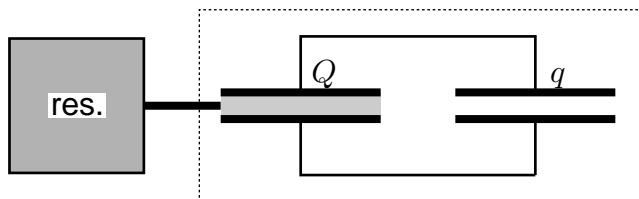


Fig. 6.3 The system, enclosed in the dashed-line box, consists of a dielectric capacitor and a vacuum capacitor in parallel, in contact with a thermal reservoir.

6.15 THERMODYNAMICS WITH E AND B FIELDS

If a substance is placed in an electric field, it becomes polarized. That is, the atoms or molecules that make up the substance develop electric dipole moments in the direction of the electric field, or, if they have permanent dipole moments, these tend to line up with the field. The dipole moment per unit volume is called the *electric polarization* and is denoted \mathbf{P} . In a similar way, if a substance is placed in a magnetic field, it develops a magnetization \mathbf{M} (a magnetic dipole moment per unit volume). The thermodynamic functions of the substance, such as the entropy or the free energy, will be affected by the degree of electric or magnetic polarization. In this section, the thermodynamic conditions that determine the equilibrium values of \mathbf{P} and \mathbf{M} will be derived. Thermodynamics in the presence of fields is a fairly subtle subject. Therefore, in order to deepen the reader’s understanding of it, the calculation for the electric field case will be carried out

twice, at different levels of sophistication. Naturally, we will obtain the same equilibrium condition by the two methods. Another reason for repeating the calculation is that the magnetic field case requires the more sophisticated method, because the simple method makes use of conserved electric charge and no equivalent magnetic charge exists.

We consider the system shown in Fig. 6.3. A slab of dielectric, of area A and thickness ℓ , lies between two capacitor plates. It is in thermal contact with a reservoir at temperature T . The capacitor plates are connected to a vacuum capacitor of capacity C_o . The system, shown by the dashed line, is composed of the two capacitors but not the reservoir. The Helmholtz free energy of a system is related to the canonical potential by the simple relation $F = -kT\phi$. Since the canonical potential is a maximum at equilibrium, it is clear that, in the equilibrium state, the value of F must be a minimum. Therefore, the equilibrium condition for the system is that the total free energy, $F = U - TS$ (where we have changed the symbol denoting the energy from E to U in order to prevent confusion with the electric field \mathbf{E}) must be a minimum in comparison with any other state to which the system might go without violating fundamental conservation laws. The free energy of the dielectric capacitor may be calculated by integrating f , the free energy per unit volume of the dielectric material (which includes the electric field energy density), over the volume of the dielectric. The free energy density of a piece of the dielectric depends on its density n and the temperature T , but it also depends on the strength of the electric field passing through it, since the existence of the field will add a field energy term and will also affect the microscopic distribution of the particles in the material. We could describe the electric field dependence by making f a function of the local electric field E , but we could also use other, equivalent, variables, such as the polarization P or the displacement field D to describe the field dependence. The most convenient formulation is obtained if f is taken as a function of n , T , and D . To calculate the total free energy of the system we must add the energy of the vacuum capacitor, which has no entropy. Thus

$$F = \ell A f(n, T, D) + \frac{q^2}{2C_o} \quad (6.95)$$

If the system is at equilibrium with the indicated charges on the plates, then F must be unchanged, to first order, by any small shift of charge dq from the dielectric capacitor to the vacuum capacitor. Thus

$$dF = \ell A \frac{\partial f}{\partial D} dD + \frac{q dq}{C_o} = 0 \quad (6.96)$$

But, by the definition of D , $D = Q/A$, and thus, $dD = dQ/A = -dq/A$, by charge conservation. This implies that

$$dF = \left(-\ell \frac{\partial f}{\partial D} + V \right) dq = 0 \quad (6.97)$$

for any infinitesimal dq , where $V = q/C_o$ is the voltage on the vacuum capacitor. We note that the voltage on the vacuum capacitor is the same as the voltage on the dielectric capacitor, which is given by $V = \ell E$, where E is the electric field within the dielectric material. We therefore obtain, as our condition for equilibrium, that the field within the dielectric is related to its free energy density by

$$E = \frac{\partial f(n, T, D)}{\partial D} \quad (6.98)$$

This equation shows that \mathbf{D} and \mathbf{E} are thermodynamically conjugate variables. Shortly it will be shown that \mathbf{H} and \mathbf{B} are also conjugate variables. These facts are really quite remarkable when one recalls that the definitions of these fields were devised by Maxwell with no consideration of thermodynamics at all.

For most materials, the displacement vector is proportional to the local electric field, the proportionality constant being ϵ , the dielectric constant of the substance. This would say that

$$\frac{\partial f(n, T, \mathbf{D})}{\partial \mathbf{D}} = \frac{\mathbf{D}}{\epsilon} \quad (6.99)$$

an equation that can be easily integrated to give

$$\begin{aligned} f(n, T, D) &= f_o(n, T) + \frac{D^2}{2\epsilon} \\ &= f_o(n, T) + \frac{1}{2}ED \end{aligned} \quad (6.100)$$

where $f_o(n, T)$ is the Helmholtz free energy density of the material with no electric field.

We will now consider a more general situation, in which the field varies from point to point. One aim of this analysis is that it will illustrate the techniques required for doing thermodynamic calculations on spatially nonuniform systems. We consider a sample occupying a volume V_S in the vicinity of some fixed charges that give rise to an electric field (see Fig. 6.4). The Helmholtz free energy of the system, $F = U - TS$, will include the electric field energy, and thus F could be written in the form (E_3 is three-dimensional Euclidean space)

$$F = \frac{1}{2}\epsilon_o \int_{E_3 - V_S} E^2 d^3\mathbf{r} + \int_{V_S} f d^3\mathbf{r} \quad (6.101)$$

where f , the Helmholtz free energy per unit volume, will vary from point to point because of the variation in the electric field strength. The restriction of the electric field integral to the region outside the dielectric material is inconvenient for the analysis. We can eliminate it by defining another function \tilde{f} , which it is best to consider as a function of n , T , and \mathbf{P} (\mathbf{P} is the polarization of the dielectric), by

$$\tilde{f}(n, T, \mathbf{P}) \equiv f + \frac{\epsilon_o}{2}E^2 \quad (6.102)$$

With this definition,

$$F = \frac{\epsilon_o}{2} \int_{E_3} E^2 d^3\mathbf{r} + \int_{V_S} \tilde{f} d^3\mathbf{r} \quad (6.103)$$

For isotropic substances, \tilde{f} depends only on the magnitude of \mathbf{P} , but for many crystalline solids it depends also on the orientation of the polarization vector with respect to the crystal axes. The electric field, in general, varies from point to point, and therefore the polarization at equilibrium would be expected to do so also. Thus the equilibrium value of the polarization is given by the vector function $\mathbf{P}(\mathbf{r})$ that minimizes the free energy defined in Eq. (6.103). This is obviously a more difficult minimization problem than any we have encountered before. It is solved by the following device.

Suppose $\mathbf{P}(\mathbf{r})$ is the function that minimizes F . Consider the change in F when we change the polarization from $\mathbf{P}(\mathbf{r})$ to $\mathbf{P}(\mathbf{r}) + \Delta\mathbf{P}(\mathbf{r})$, where $\Delta\mathbf{P}(\mathbf{r})$ is any extremely small vector function of \mathbf{r} . Call the change ΔF . Of course, if we change the polarization, then the electric field will also undergo a change from the equilibrium electric field $\mathbf{E}(\mathbf{r})$ to some new electric field, $\mathbf{E}(\mathbf{r}) + \Delta\mathbf{E}(\mathbf{r})$. Thus

$$\begin{aligned} \Delta F &= \frac{\epsilon_o}{2} \int_{E_3} [(\mathbf{E} + \Delta\mathbf{E})^2 - E^2] d^3\mathbf{r} + \int_{V_S} [\tilde{f}(\mathbf{P} + \Delta\mathbf{P}) - \tilde{f}(\mathbf{P})] d^3\mathbf{r} \\ &= \epsilon_o \int_{E_3} \mathbf{E} \cdot \Delta\mathbf{E} d^3\mathbf{r} + \int_{V_S} \frac{\partial \tilde{f}}{\partial \mathbf{P}} \cdot \Delta\mathbf{P} d^3\mathbf{r} \end{aligned} \quad (6.104)$$

where we have used the fact that $\Delta\mathbf{P}$ is very small to neglect all higher-order terms in the small quantities $\Delta\mathbf{P}$ and $\Delta\mathbf{E}$, and where

$$\frac{\partial \tilde{f}}{\partial \mathbf{P}} \cdot \Delta\mathbf{P} \equiv \frac{\partial \tilde{f}}{\partial P_x} \Delta P_x + \frac{\partial \tilde{f}}{\partial P_y} \Delta P_y + \frac{\partial \tilde{f}}{\partial P_z} \Delta P_z \quad (6.105)$$

In the Mathematical Appendix it is shown, using the equations of electrostatics, that

$$\epsilon_o \int_{E_3} \mathbf{E} \cdot \Delta\mathbf{E} d^3\mathbf{r} = - \int_{V_S} \mathbf{E} \cdot \Delta\mathbf{P} d^3\mathbf{r} \quad (6.106)$$

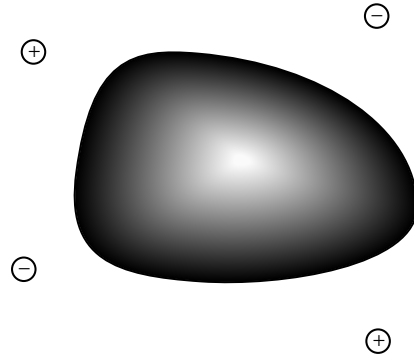


Fig. 6.4 A piece of dielectric material is in the vicinity of some fixed electric charges.

Therefore,

$$\Delta F = \int_{V_S} \left(\frac{\partial \tilde{f}}{\partial \mathbf{P}} - \mathbf{E} \right) \cdot \Delta \mathbf{P} d^3 \mathbf{r} \quad (6.107)$$

It is clear that ΔF cannot be negative, because \mathbf{P} was defined as that polarization that minimized F . But, if for some $\Delta \mathbf{P}(\mathbf{r})$, ΔF were positive, then for the change, $-\Delta \mathbf{P}(\mathbf{r})$, ΔF would be negative, which is impossible. Thus ΔF cannot be negative nor positive (and thus must be zero) for any vector function $\Delta \mathbf{P}(\mathbf{r})$. This is possible only if

$$\frac{\partial \tilde{f}(n, T, \mathbf{P})}{\partial \mathbf{P}} = \mathbf{E}(\mathbf{r}) \quad (6.108)$$

which is thus the desired equilibrium condition for the polarization of a material in an electric field.

That the two equations that have been obtained for the equilibrium electric field are equivalent is a consequence of the electrostatic identity defining the polarization, $\mathbf{P} = \mathbf{D} - \epsilon_o \mathbf{E}$. (See Problem 6.20.)

6.16 THE MAGNETIZATION

The derivation of the equilibrium condition for the magnetization of a substance in an external magnetic field follows closely the analysis for the electric polarization. We consider a system that is composed of two parts, a ferromagnet substance that occupies the region \mathbf{V}_F and another substance that occupies the region \mathbf{V}_S . (A ferromagnetic substance is one that has a net magnetization at equilibrium.) The combined region, $\mathbf{V}_F \cup \mathbf{V}_S$, is called \mathbf{V}_C . This extra complication is necessary because there is no magnetic equivalent to the fixed electric charges that were used in the last section.

As before, the Helmholtz free energy contains a term describing the field energy and a term describing the thermodynamic free energy of the specimen.

$$\begin{aligned} F &= \frac{1}{2\mu_o} \int_{E_3 - \mathbf{V}_C} B^2(\mathbf{r}) d^3 \mathbf{r} + \int_{\mathbf{V}_C} f d^3 \mathbf{r} \\ &= \frac{1}{2\mu_o} \int_{E_3} B^2(\mathbf{r}) d^3 \mathbf{r} + \int_{\mathbf{V}_C} \tilde{f}(n, T, \mathbf{M}) d^3 \mathbf{r} \end{aligned} \quad (6.109)$$

We follow the analysis of the last case exactly, making use of the following theorem, derived in the Mathematical Appendix.

$$\frac{1}{\mu_o} \int_{E_3} \mathbf{B}(\mathbf{r}) \cdot \Delta \mathbf{B}(\mathbf{r}) d^3 \mathbf{r} = \int_{\mathbf{V}_C} \mathbf{B}(\mathbf{r}) \cdot \Delta \mathbf{M}(\mathbf{r}) d^3 \mathbf{r} \quad (6.110)$$

Notice the difference in sign between this equation and Eq. (6.106). Taking into account this sign difference, we obtain, by methods analogous to those used in the electrostatic case, the relation that

$$\Delta F = \int_{\mathbf{V}_C} \left(\frac{\partial \tilde{f}}{\partial \mathbf{M}} + \mathbf{B} \right) \cdot \Delta \mathbf{M} d^3 \mathbf{r} = 0 \quad (6.111)$$

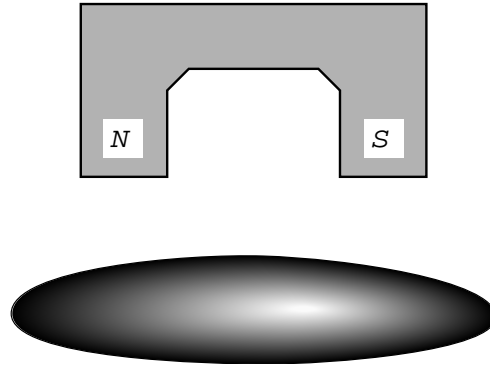


Fig. 6.5 A piece of material is in the vicinity of a ferromagnet.

for all possible changes in the magnetization. Thus the equation for the magnetic field \mathbf{B} at equilibrium is

$$\mathbf{B}(\mathbf{r}) = -\frac{\partial \tilde{f}}{\partial \mathbf{M}} \quad (6.112)$$

This equation is valid for both ferromagnetic and nonferromagnetic substances. It is the magnetic analog of Eq. (6.108). To obtain the magnetic analog of Eq. (6.98), we recall that the relationship connecting the magnetization \mathbf{M} , the magnetic field \mathbf{B} , and the magnetic displacement \mathbf{H} is

$$\mathbf{H} = \frac{1}{\mu_o} \mathbf{B} - \mathbf{M} \quad (6.113)$$

From this, and the fact that $f = \tilde{f} + B^2/2\mu_o$, we obtain

$$df = d\tilde{f} + \frac{1}{\mu_o} \mathbf{B} \cdot d\mathbf{B} = -\mathbf{B} \cdot d\mathbf{M} + \frac{1}{\mu_o} \mathbf{B} \cdot d\mathbf{B} = \mathbf{B} \cdot d\mathbf{H} \quad (6.114)$$

which implies that, if we write the free energy per unit volume (including the magnetic field energy) as a function of n , T , and \mathbf{H} , then the equilibrium magnetic field is given by

$$\mathbf{B}(\mathbf{r}) = \frac{\partial f(n, T, \mathbf{H})}{\partial \mathbf{H}} \quad (6.115)$$

PROBLEMS

6.1 In a reaction vessel of volume 0.1 m^3 at a temperature of 700 K , 4×10^{-4} moles of H_2 , 2×10^{-4} moles of I_2 , and 2.09×10^{-3} moles of HI (hydrogen iodide) are in equilibrium with respect to the reaction $\text{H}_2 + \text{I}_2 \leftrightarrow 2\text{HI}$. If an additional 10^{-3} moles of HI are added to the vessel, which is kept at constant temperature, what will be the amounts of the three chemical species when equilibrium is reestablished?

6.2 Suppose the equilibrium constant for the reaction $A \leftrightarrow 2B$ is $2 \times 10^{-4} \text{ m}^{-3}$ and that for the reaction $B \leftrightarrow C$ is 0.3 . What is the equilibrium constant for the reaction $A \leftrightarrow 2C$?

6.3 When 0.1 mole of HI is placed in a reaction vessel kept at 45° C , 22% of it decomposes by the reaction, $2\text{HI} \leftrightarrow \text{H}_2 + \text{I}_2$. If another 0.1 mole of H_2 is added to the vessel, how many moles of HI will there be at equilibrium?

6.4 At 25° C , with equal molar densities of H_2O (gas) and H_2 , the reaction $\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}$ is at equilibrium when the densities of CO and CO_2 are in the ratio, $n_{\text{CO}}/n_{\text{CO}_2} = 2.57 \times 10^{-6}$. Going from left to right, the reaction absorbs energy at the rate of 28.5 kilojoules/mole. What would be the equilibrium constant for the reaction at 500° C ?

6.5 An ideal gas molecule has two possible internal energy states, with energies ε_a and ε_b . (a) Consider the transition between the two states as a chemical reaction, $a \leftrightarrow b$, and calculate the equilibrium constant as a function of T . (b) For this 'chemical reaction', verify Van't Hoff's law.

6.6 A pure dissociation reaction, $AB \leftrightarrow A + B$, takes place at fixed volume in a gas that initially contains only AB molecules at a density of n_o . The degree of dissociation is defined as the ratio of dissociated A atoms to the total density of A atoms. That is, $r \equiv n_A/(n_A + n_{AB})$. Show that $r = (\sqrt{\gamma + 1/4} - 1/2)/\gamma$, where $\gamma = n_o/K$ and K is the equilibrium constant of the reaction.

6.7 Show that, in a partially ionized hydrogen gas, the ratio of the electron density to the total particle density, $n_{\text{tot}} = n_{e^-} + n_{\text{H}^+} + n_{\text{H}}$, is given by $n_{e^-}/n_{\text{tot}} = \sqrt{\lambda(\lambda + 1)} - \lambda$, where $\lambda = e^{-\beta\varepsilon_o}/n_{\text{tot}}\lambda_e^3$.

6.8 Equation (6.15) gives the change in the equilibrium constant with respect to temperature at fixed volume. For gas reactions in a reaction vessel of fixed volume, this is useful, but for reactions in aqueous solution, what is desired is $(\partial K/\partial\beta)_p$. Show that, at fixed pressure, Van't Hoff's law has the same form, but the heat of reaction W must be defined by [compare with Eq. (6.11)]

$$E(N_A, N_B, N_R, \beta, p) = E(N_A + \Delta N_A, N_B + \Delta N_B, N_R + \Delta N_R, \beta, p) + kW + p\Delta V$$

where ΔV is the change in the volume of the system when k reactions take place at fixed pressure.

6.9 The molar volume of water is 18.02 cm^3 and that of ice is 19.63 cm^3 at 0° C and one atmosphere. The heat of fusion of the transition is 6000 Joules per mole. Taking these quantities as constants, determine the melting temperature at a pressure of 100 atmospheres.

6.10 Prove that the molar Gibbs free energy of any simple substance is equal to its chemical potential.

6.11 Figure 6.6 shows the constant pressure specific heat of hydrogen sulfide, maintained at a pressure of one atmosphere, from 0 K to its boiling point at 212.8 K . In that temperature interval, it passes through three different solid phases and a liquid phase. The enthalpy changes (in calories per mole) at the phase transitions are shown in the figure. Reasonable approximations to $C_p(T)$ in the four temperature intervals are

$$C_p = 0.0936T, \quad 0 < T < 103.5 \text{ K}$$

$$C_p = 11.05 + 0.135(T - 103.5), \quad 103.5 < T < 126.2 \text{ K}$$

$$C_p = 13.23 + 0.0066(T - 126.2) + 0.00022(T - 126.2)^2, \quad 126.2 < T < 187.6 \text{ K}$$

$$C_p = 16.2 + 0.005(T - 187.6), \quad 187.6 < T < 212.8 \text{ K}$$

Draw a graph of the entropy per mole at one atmosphere, as a function of T in the temperature range, $0 < T < 212.8 \text{ K}$.

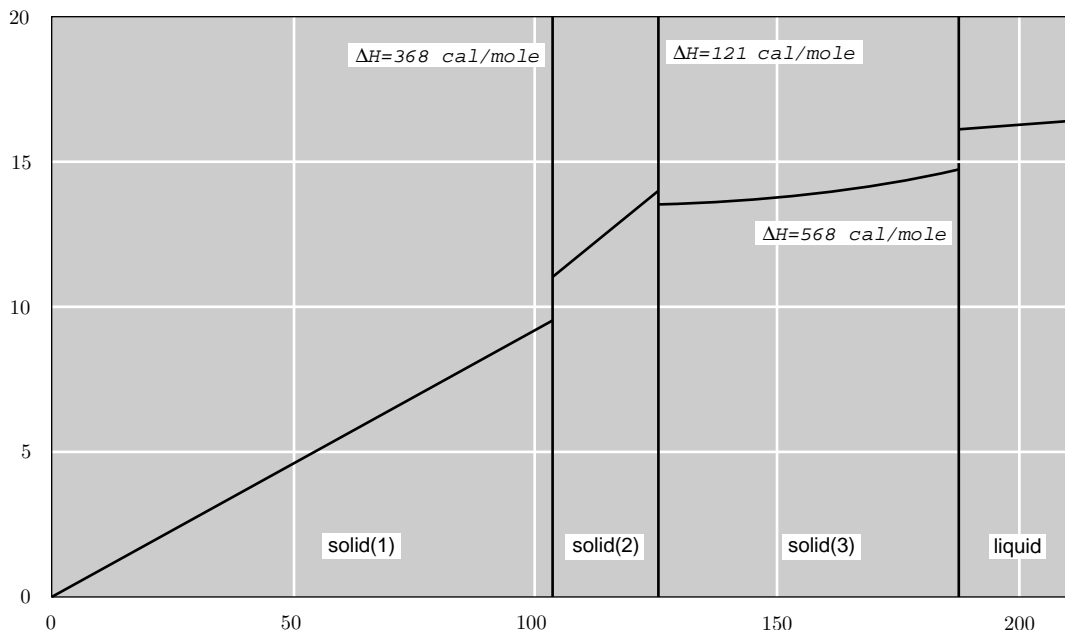


Fig. 6.6 C_p for one mole of HS (in calories) as a function of temperature (in K). The enthalpy changes at the phase transitions are indicated.

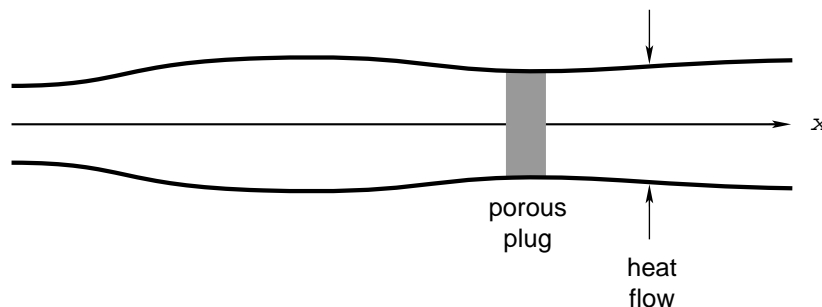


Fig. 6.7 A fluid flows in the x -direction through a pipe of varying cross-section.

6.12 Figure 6.7 shows a fluid flowing through a tube of varying cross-sectional area. Assume that the flow is viscous and that the tube contains obstructions, such as the porous plug shown, and that heat is being added and leaking away. Assume also that everything, including the velocity at each point in space, is *constant in time*. Let $h(x)$ be the enthalpy per mole of the fluid at point x , and $v(x)$ be the flow velocity at x . Show that

$$h(x_2) + \frac{1}{2}mv^2(x_2) = h(x_1) + \frac{1}{2}mv^2(x_1) + Q$$

where Q is the net rate at which heat is being added to the fluid *per mole* between points x_1 and x_2 and m is the molar mass of the fluid.

6.13 The flow of a gas through a porous plug is called a Joule-Thompson process. It is of great importance in practical refrigeration methods and is usually used at some point in the process of liquifying gases, such as nitrogen and helium. Consider the process shown in Fig. 6.8. Assume that the kinetic energy associated with the macroscopic flow velocity of the gas is negligible in comparison with the internal energy of the gas. Then, by the result of Problem 6.12, the enthalpy per mole is unchanged in flowing through the plug. Assume that the pressure and temperature differentials, Δp and ΔT , are small. Show that cooling occurs only if the initial temperature of the gas satisfies the relation $\beta_p T > 1$. [β_p is defined in Eq. (6.63).] The curve $p(T)$ that limits the region in the p - T plane in which this inequality is satisfied (defined by $\beta_p T = 1$)

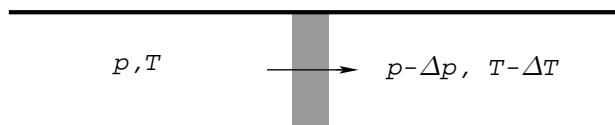


Fig. 6.8 In flowing through the porous plug the fluid undergoes a small drop in pressure and a small change in temperature.

is called the Joule–Thompson *inversion curve*.

6.14 The adiabatic coefficient of thermal expansion is defined by $V\beta_S = (\partial V/\partial T)_S$. Show that $\beta_S - \beta_p = -\kappa_T C_p / TV\beta_p$.

6.15 Let $L(T)$ be the latent heat per mole at a transition from phase A to phase B . Show that $T d(L/T)/dT = C_p(B) - C_p(A)$, where $C_p(A)$ and $C_p(B)$ are the constant pressure molar specific heats of the two phases close to the transition line.

6.16 A volume V_l of liquid water and a volume V_g of steam are in equilibrium at pressure p in a thermally insulated cylinder, topped by a piston. The pressure is increased a small amount, dp . Obtain an expression for the change in volume, dV . Ignore the compressibility of the liquid (but not that of the gas) and the molar volume of the liquid in comparison with that of the gas.

6.17 Express the Gibbs–Duhem relation in terms of the variables μ , T , and p .

6.18 In an isotropic substance the vector variables \mathbf{P} and \mathbf{E} may be replaced by their scalar magnitudes, P and \mathcal{E} . (The symbol, \mathcal{E} , is used to avoid confusion with the energy.) The molar entropy and the polarization can be written as functions of the particle density, the temperature, and \mathcal{E} . Show that $\partial s(n, T, \mathcal{E})/\partial \mathcal{E} = \partial P(n, T, \mathcal{E})/\partial T$.

6.19 A parallel plate capacitor filled with some dielectric is connected to a very large external capacitor at voltage V . The heat capacity of the parallel plate capacitor in this situation is found to be C_V , where in this context the subscript V stands for constant voltage, not volume, although one should assume throughout this problem that any volume change is negligible. The plate capacitor is now disconnected from the external capacitor. Its heat capacity is measured again and found to be C_Q , where the subscript Q means constant charge. Show that $C_V > C_Q$.

6.20 Equation (6.98) implies that, at constant n and T , $df = \mathbf{E} \cdot d\mathbf{D}$. Use this, and the definitions, $\mathbf{P} = \mathbf{D} - \epsilon_o \mathbf{E}$ and $\tilde{f} = f - \epsilon_o E^2/2$, to show that, at constant n and T , $d\tilde{f} = \mathbf{E} \cdot d\mathbf{P}$, which is equivalent to Eq. (6.108).

6.21 Equation (4.78) is equivalent to the equation $P = -\partial f'(n, T, E)/\partial E$, where $f' = -kT\phi/V$. Equation (6.108) states that $E = \partial \tilde{f}(n, T, P)/\partial P$. Show that \tilde{f} and f' are related by a Legendre transformation from the variable P to the variable E .