Exercises on Ch.2 Manipulation of thermodynamic quantities

2.2 Internal variables at equilibrium

2.4 Experimental conditions

2.5 Notation for partial derivatives

2.6 Use of various derivatives

2.7 Comparison between C_V and C_P

2.8 Change of independent variables

2.9 Maxwell relations

2.2 Internal variables at equilibrium

Exercise 2.2.1

At high temperatures, H₂ gas may partially dissociate into H atoms. The following expression can be used for the Gibbs energy of a system which initially contained one mole of H₂ molecules: $G = (1 + \xi)RT\ln[P/(1 + \xi)] + (1 - \xi)[^{\circ}G_{H2} + RT\ln(1 - \xi)] + 2\xi[^{\circ}G_{H} + RT\ln(2\xi)]$. Here, ξ is the fraction of H₂ molecules which have dissociated into free H atoms, and $^{\circ}G_{H2}$ and $^{\circ}G_{H}$ are the Gibbs energies of one mole of pure H₂ and H, respectively, at a pressure equal to the unit used for pressure. Show how V can be calculated under freezing-in conditions at constant T and P. Then derive an expression for the equilibrium value of ξ and show how V can be calculated under equilibrium conditions.

Hint

It is convenient to introduce the equilibrium constant for the reaction $H_2 \Leftrightarrow 2H, K = \exp[(2^{\circ}G_{\rm H} - {^{\circ}G_{\rm H2}})/RT]$.

Solution

Freezing-in conditions: $V = (\partial G/\partial P)_{T,\xi} = (1 + \xi)RT/P$ for any constant value of ξ . *Equilibrium conditions:* $-D = (\partial G/\partial \zeta)_{T,P} = RT\ln P - RT(1 + \xi)/(1 + \xi) - RT\ln(1 + \xi) - {}^{\circ}G_{H2} - RT\ln(1 - \xi) + RT(1 - \xi)/(1 - \xi)(-1) + 2{}^{\circ}G_{H} + 2RT\ln(2\xi) + 2RT\xi/\xi = 0$ gives $(1 - \xi^2)4P\xi^2 = K$ and $\xi = 1/\sqrt{1 + 4PK}$ at equilibrium. This ξ value could be inserted in the expression for *G* and $V = (\partial G/\partial P)_T$ could then be evaluated. However, since $(\partial G/\partial \zeta)_{T,P} = 0$ we can directly use the expression derived for the frozen-in case, with the equilibrium value of ξ inserted. We thus obtain $V = (RT/P)(1 + 1/\sqrt{1 + 4PK})$.

Exercise 2.2.2

According to a simple model, the internal energy of a solid metal at absolute zero can be described with an expression of the form $U/N = k_1(V/N)^{-2/3} - k_2(V/N)^{-1/3}$ where N is the number of moles in the volume V. The equilibrium volume is then calculated from the minimum of U obtained from $d(U/N)/d(V/N) = (2/3)k_1(V/N)^{-5/3} + (1/3)k_2(V/N)^{-4/3} = 0$ giving $V/N = (2k_1/k_2)^3$. This procedure may look incorrect because S and V are supposed to be constant when equilibrium is calculated by minimizing U. Discuss whether it may be correct, nevertheless.

Hint

Equilibrium should be calculated with respect to an *internal* variable, ξ , using $(\partial U/\partial \xi)_{s,v} = 0$ and V (or V/N) is regarded as ξ in the above calculation. It must be different from the V quantity which is kept constant. Try to define the nature of the two volumes by considering one mole of the metal contained in a constant volume V. What will happen?

Solution

We have no problem with *S*, which we can put to zero at absolute zero. Identifying ξ with *V* in the expression for *U* and denoting the volume of the container by V_c , we can rewrite $(\partial U/\partial \xi)_{s,v}$ as $(\partial U/\partial V)_{s,vc}$. Suppose there is no atmosphere in the container and neglect the vapour pressure of the metal itself. The metal is then free to adjust its volume *V* (i.e. ξ) without affecting the volume of the whole system, V_c (i.e. an external state variable) and without affecting the number of atoms in the system. *N* should be interpreted as the number of atoms in the volume V_{c_1} and *N* is thus constant. The calculation is then correct.

2.4 Experimental conditions

Exercise 2.4.1

Find the conditions for which $T(\partial S/\partial T)_v$ is equivalent to $C_v = (\partial U/\partial T)_v$.

Hint

Start from the basic form of the combined law.

 $dU = TdS - PdV - Dd\xi$. Under constant V we get dU = TdS and $(\partial U/\partial T)_v = T(\partial S/\partial T)_v$ if $Dd\xi = 0$. This occurs under two different conditions. One is D = 0, so-called reversible conditions. The change of T is slow enough to make ξ adjust to equilibrium all the time. The other is $d\xi = 0$, so-called freezing-in conditions. The change is so rapid that there is no internal reaction. For clarity we could write this case as $(\partial U/\partial T)_{v,\xi} = T(\partial S/\partial T)_{v,\xi}$. Of course, it is always true if there is no possible internal process in the system.

Exercise 2.4.2

It is well known that S can increase spontaneously towards a maximum if U and V are kept constant. Find another condition under which S can increase spontaneously towards a maximum. Then, discuss how the two kinds of conditions can be realized experimentally.

Hint

We can use any form of the combined law which contains d*S*, then use the first law in order to examine the experimental conditions.

Solution

 $dH = TdS + VdP - Dd\xi$ can be written as $TdS = dH - VdP + Dd\xi$ and S may thus increase spontaneously towards a maximum if H and P are constant as well as if U and V are kept constant. The first law gives dU = dQ - PdV and the condition of constant U and V may thus be realized experimentally by keeping dQ and dV equal to zero, i.e. by using adiabatic and isochoric conditions. By introducing H into the first law we get dH = d(U + PV) = dQ - PdV + PdV + VdP = dQ + VdP. The condition of constant H and P can thus be realized experimentally by keeping dQ and dP equal to zero, i.e. by using adiabatic and isobaric conditions.

In fact, *S* will increase spontaneously towards a maximum under all adiabatic conditions. The second law gives directly $dS = dQ + Dd\xi = Dd\xi > 0$ for all spontaneous processes.

Exercise 2.4.3

One mole of a fluid at T_1, P_1 is compressed adiabatically to P_2 . Discuss how one can calculate the work done on the system if one knows the properties of the system.

Hint

The problem may look like a simple first-law problem. However, it is not well defined. We must make some assumption regarding the process of compression in addition to its being adiabatic. Make the assumption that would give the simplest calculation.

Suppose the experiment is made under reversible conditions in addition to adiabatic conditions. Then the second law gives $TdS = dQ + Dd\xi = 0$ and S is constant. If we had an equation of state S = S(T,P), then we could calculate the new T from the new P and the old T and P. If we also had an equation of state U = U(T,P), then we could calculate ΔU between the two states and that would be equal to the work done on the system because the first law gives dU = dQ + dW = dW.

2.5 Notation for partial derivatives

Exercise 2.5.1

How should H_{PP} be interpreted?

Solution

S and P are the natural variables of H and H_{PP} thus means $(\partial^2 H/\partial P^2)_{s,\xi}$ or $(\partial^2 H/\partial P^2)_s$. In the latter case ξ is a dependent variable which is continuously adjusted to equilibrium. In order to interpret H_{PP} one would need to know the conditions.

2.6 Use of various derivatives

Exercise 2.6.1

Prove the following relation which is known to be a very useful equation $(\partial U/\partial V)_{T} = T(\partial P/\partial T)_{V} - P$.

Hint

Since V and T are used as variables, express U in terms of F which has V and T as its natural variables. Remember that $(\partial P/\partial T)_{V} = -F_{VT} = (\partial S/\partial V)_{T}$.

Solution

 $U = F + ST; (\partial U/\partial V)_{\rm T} = (\partial F/\partial V)_{\rm T} + T(\partial S/\partial V)_{\rm T} = -P + T(\partial P/\partial T)_{\rm V}.$

Exercise 2.6.2

Express the effect of adiabatic compression on the temperature in terms of directly measurable material properties. Suppose there is no entropy producing internal process.

Hint

Remember from Section 2.4 that a reversible and adiabatic process is also isentropic. One should thus start by expressing dS as a function of dP and dT.

Since $S = -(\partial G / \partial T)_P = -G_T$ one obtains $dS = -G_{TP}dP - G_{TT}dT = -V\alpha dP + (C_P / T)dT$. Thus, dS = 0 yields $(dT / dP)_{adiab.} = TV\alpha / C_P$. This result describes the so-called thermoelastic effect. α is usually positive and a pressure increase will then cause the temperature to rise. However, there are some materials where α is negative and the temperature will sink. For a material with negative α the temperature will thus sink although the work of compression is positive. It is evident that the effect on temperature is not related to the work of compression.

Exercise 2.6.3

From the result of the previous exercise, $(dT/dP)_{adiab.} = TV\alpha/C_P$, it would seem that the thermoelastic effect is independent of the compressibility. The equation seems to predict that the temperature should change with P even if the compressibility is zero, which may seem surprising because one can see no effect of the increased P on the structure of the material. The distances between atoms have not changed. This seems like a paradox. Try to find an explanation.

Hint

Check carefully if the thermoelastic effect is really independent of the compressibility.

Solution

 C_V is a more fundamental material property than C_P because it only concerns what happens inside the material when heated. It may seem reasonable that C_V is fairly independent of the compressibility, κ_T . Eq. 2.34 yields $C_P = C_V + TV\alpha^2 / \kappa_T$ and C_P would thus go to infinity when κ_T goes to zero whereas C_V does not. The thermoelastic effect will also go to zero and there is no paradox. It should be better to write the thermoelastic effect as $(dT/dP)_{adiab} = 1/(C_V / TV\alpha + \alpha / \kappa_T)$.

Exercise 2.6.4

It is well known that the heat capacity at constant volume is defined as dQ/dT at constant V. Another important quantity is defined as dQ/dV at constant T. It is sometimes called the latent heat of volume change. Derive a general expression for this new quantity in terms of state variables.

Hint

Since the variables are V and T, it is convenient to use F and its derivatives. Start with the first law, then use $U = F + ST = F - TF_{T}$.

dQ = dU + PdV; $(\partial Q/\partial V)_T = (\partial U/\partial V)_T + P = F_V - TF_{TV} + P = -TF_{TV}$. Using the hint in the preceding problem, the result can also be expressed as $T(\partial S/\partial V)_T$ or $T(\partial P/\partial T)_V$.

Exercise 2.6.6

It is well known that G has a minimum at equilibrium under constant T and P but F has a minimum at equilibrium under constant T and V. That being so, what is wrong in the following derivation?

Consider V as a function of P and T,

 $dV = (\partial V/\partial P)_{T}dP + (\partial V/\partial T)_{p}dT = -V\kappa_{T}dP + V\alpha dT$ $dF = -PdV - SdT - Dd\xi = PV\kappa_{T}dP - (S + PV\alpha)dT - Dd\xi$ $(\partial F/\partial\xi)_{T,P} = -D$

If this derivation were correct, it would seem that there could be a spontaneous process under constant P and T until F has reached a minimum, not G.

Hint

We are considering a system with a possible internal process. We must then include ξ among the state variables and realize that the volume depends upon the ξ value.

Solution

We want to replace dV in $dF = -PdV - SdT - Dd\xi$ and instead introduce dP. It is evident that we must then consider V as a function of the new set of variables P, T, ξ : $dV = (\partial V/\partial P)_{T,\xi}dP + (\partial V/\partial T)_{P,\xi}dT + (\partial V/\partial \xi)_{T,P}d\xi = -V\kappa_T dP + V\alpha dT + (\partial V/\partial \xi)_{T,P}d\xi$ and here K_T and α must be determined at constant ξ . We now get $dF = PV\kappa_T dP - (S + PV\alpha)dT - [D + P(\partial V/\partial \xi)_{T,P}]d\xi$. At constant $T,P: D + P(\partial V/\partial \xi)_{T,P} = -(\partial F/\partial \xi)_{T,P}$ and $-D = [\partial (F + PV)/\partial \xi]_{T,P}$ $= (\partial G/\partial \xi)_{T,P}$.

2.7 Comparison between C_V and C_P

Exercise 2.7.1

Calculate the heat flow into a system in two cases:

- (a) Heating from T_1 to T_2 under constant V.
- (b) Heating from T_1 to T_2 under constant *P* and then compression back to the initial volume under constant T_2 .

Suppose the system is an ideal classical gas for which PV = RT and U = A + BT.

Hint

Use the first law in all cases.

Solution

(a) dQ = dU + PdV = dU; $Q = \Delta U = B(T_2 - T_1)$. (b₁) dQ = dU + PdV; $Q_1 = \Delta U + P_1\Delta V = B(T_2 - T_1) + P_1(V_2 - V_1)$. (b₂) dQ = dU + PdV; $Q_2 = \Delta U + \int PdV = 0 + \int (RT_2/V)dV = RT_2 \ln(V_1/V_2)$

where $V_1 = RT_1/P_1$; $V_2 = RT_2/P_1$. Therefore, $\Sigma Q = B(T_2 - T_1) + R(T_2 - T_1) + RT_2 \ln(T_1/T_2)$. For small $T_2 - T_1$: $T_2 \ln(T_1/T_2) = T_2 \ln[1 + (T_1 - T_2)/T_2] \cong T_1 - T_2$, and $\Sigma Q \cong (B + R - R)(T_2 - T_1) = B(T_2 - T_1)$. (Same as for (a).)

2.8 Change of independent variables

Exercise 2.8.1

From $\gamma = \alpha V/C_V \kappa_T$, show that $\gamma = \alpha V/C_P \kappa_S$, i.e. show that $C_V \kappa_T = C_P \kappa_S$.

Hint

 $\kappa_{\rm s} = -(\partial V/\partial P)_{\rm s}/V$. Change all the derivatives to G of T and P. Use the expressions of C_P and C_V in terms of such derivatives. C_V and κ_T were given in Section 2.6.

Solution

$$-V\kappa_{S} = (\partial V / \partial P)_{S} \begin{vmatrix} \partial V / \partial P & \partial V / \partial T \\ \partial S / \partial P & \partial S / \partial T \end{vmatrix} / \begin{vmatrix} \partial P / \partial P & \partial P / \partial T \\ \partial S / \partial P & \partial S / \partial T \end{vmatrix}$$
$$= (\partial V / \partial P)_{T} - (\partial V / \partial T)_{P} (\partial S / \partial P)_{T} / (\partial S / \partial T)_{P} = G_{PP} - G_{PT}G_{TP} / G_{TT}$$

But $C_P = -TG_{TT}$ and $V = G_P$. Thus $C_P \kappa_S = T(G_{TT}G_{PP} - G_{TP}^2)/G_P$. From expressions for C_V and κ_T in Section 2.6 we get $C_V \kappa_T = T(G_{TP}^2 - G_{TT}G_{PP})(1/G_{PP})(-G_{PP}/G_P)$ which yields $C_P \kappa_S$.

2.9 Maxwell relations

Exercise 2.9.1

Show that $dS = (C_v/T)dT + (\alpha/\kappa_T)dV$.

Hint

We want to show that $C_V/T = (\partial S/\partial T)_V$ and $\alpha/\kappa_T = (\partial S/\partial V)_T$. The first relation is obtained from the second law under reversible conditions. The second relation is obtained from the definitions of α and κ_T in derivatives of *G* after some manipulation involving the last equation derived in Section 2.8 and a Maxwell relation.

Solution

Under reversible conditions we get dQ = TdS; $C_v = (dQ/dT)_v = T(\partial S/\partial T)_v$. From the definitions of α and κ_T we get $\alpha/\kappa_T = (\partial V/\partial T)_P/[-(\partial V/\partial P)_T] = (\partial P/\partial T)_v = (\partial S/\partial V)_T$ and thus $dS = (C_v/T)dT + (\alpha/\kappa_T)dV$.

Exercise 2.9.2

Evaluate the thermal expansivity at absolute zero for a substance obeying the third law.

Hint

According to the third law, *S* approaches the same value at absolute zero for all ordered states of a substance. The limiting *S* value is not only independent of the crystalline structure but also of the pressure, $(\partial S/\partial P)_{T=0} = 0$.

Solution

 $\alpha = (\partial V/\partial T)_{P}/V$. Since V and P are conjugate variables, we can use a Maxwell relation, $\alpha = (\partial^2 G/\partial P \partial T)/V = -(\partial S/\partial P)_{T}/V = 0$ at T = 0.

Exercise 2.9.3

Transform $(\partial H/\partial P)_{T}$ using a Maxwell relation.

Hint

In order to introduce H as a conjugate variable to T (or rather 1/T) in the combined law, one should use the entropy scheme, presented in Section 1.12.

Solution

From the entropy scheme we get d(G/T) = Hd(1/T) + (V/T)dP. Thus, $(\partial H/\partial P)_T = (\partial H/\partial P)_{1/T} = (\partial [V/T]/\partial [1/T])_P = V - T(\partial V/\partial T)_P$.