

## CHAPTER 12 FREE ENERGY

### 12.1 *Review of Internal Energy and Enthalpy*

We are by now familiar with the equations

$$dU = TdS - PdV \quad \text{and} \quad dH = TdS + VdP,$$

and with the ideas that the increase in the internal energy is the heat added at constant volume and the increase in enthalpy is the heat added at constant pressure, and that  $U$  is constant in an adiabatic isochoric process and  $H$  is constant in an adiabatic isobaric process. I am now going to examine these equations and statements a bit more critically. In particular I am going to consider that there may be several types of configuration work involved in addition to just  $PdV$  work of compression or expansion.

The First Law of thermodynamics is  $dU = dQ + dW$ .

The work done on a system may comprise an irreversible component  $dW_I$  (such as stirring with a paddle, or forcing an electric current through a resistor) plus some reversible components  $dW_R$ . The irreversible component is dissipated as heat and is tantamount to adding heat to the system. The heat and the irreversible work contribute to the increase in entropy of the system, according to  $dS = (dQ + dW_I)/T$ . Thus we have  $dQ = TdS - dW_I$ .

The reversible component of the work may consist of work done in compressing the system,  $-PdV$ , but there may also be other kinds of work, such as the work required to create new area,  $\Gamma d\sigma$ , or the work required to twist a rod,  $\tau d\theta$ , or the work required to charge a battery,  $\mathcal{E}dq$ , or the work required to magnetize a specimen,  $BdM$ , and perhaps others. In general the expression for each of these forms of reversible work is of the form  $XdY$ , where  $X$  is an intensive state variable and  $Y$  is an extensive state variable. All of these forms of nondissipative work can collectively be called *configuration work*.

The total work done on the system is therefore of the form

$$dW = dW_I - PdV + \sum XdY. \quad 12.1.1$$

The first law therefore takes the form

$$dU = dQ + dW_I - PdV + \sum XdY. \quad 12.1.2$$

If the system is held at constant volume (e.g. in a pressure cooker or in an autoclave), then no  $PdV$  work of expansion or compression is done. And if no other sort of work is

done either (either non- $PdV$  reversible work or irreversible work  $dW_I$ ) then the increase in internal energy of the system is just equal to the heat added to it.

Enthalpy is defined as  $H = U + PV$ , so that  $dH = dU + PdV + VdP$ . From this, we obtain

$$dH = dQ + dW_I + VdP + \sum XdY. \quad 12.1.3$$

If heat is added to a system at constant pressure, then the system expands and does external work. However, provided that the pressure is held constant and if no other sort of work is done either (either non- $PdV$  reversible work or irreversible work  $dW_I$ ) then the increase in the enthalpy of the system is just equal to the heat added to it.

In summary, the well-known equations  $dU = TdS - PdV$  and  $dH = TdS + VdP$  are valid for reversible and for irreversible processes, provided that the only nondissipative work is  $PdV$  work; but in general, if there are other types of work being done (e.g.  $\Gamma d\sigma$ , or  $\tau d\theta$ , etc.), the required relations are

$$dU = TdS - PdV + \sum XdY \quad 12.1.4$$

and 
$$dH = TdS + VdP + \sum XdY. \quad 12.1.5$$

## 12.2 Free Energy

We shall be learning that there are two sorts of *free energy*.

There is the *Helmholtz free energy*. Commonly used symbols for this are  $A$  (from the German *die Arbeit* – work) or  $F$ .

And there is the *Gibbs free energy*. Commonly used symbols for this are  $G$  – or  $F$  !

It is unfortunate that some writers will use simply the term "free energy", using the symbol  $F$ , without specifying which, or even giving evidence that they are aware of the difference. I have seen the symbol  $F$  used about equally often for Helmholtz, Gibbs or unspecified free energies.

In these notes I shall use the symbol  $A$  for the Helmholtz free energy and  $G$  for the Gibbs free energy, and I shall avoid the symbol  $F$ .

### 12.3 Sorry – there is no Section 12.3

I don't want to re-number the subsequent sections, in case I have referred to them by number in future chapters. So let's just leave this one blank.

### 12.4 Helmholtz Free Energy

The *Helmholtz free energy*  $A$  is defined as

$$A = U - TS. \quad 12.4.1$$

As when we first defined enthalpy, this doesn't seem to mean much until we write it in differential form:

$$dA = dU - TdS - SdT. \quad 12.4.2$$

On substitution from equation 12.1.6 ( $dU = TdS - PdV + \sum XdY$ ), this becomes

$$dA = -SdT - PdV + \sum XdY. \quad 12.4.3$$

This tells us that in an isothermal process (in which  $dT = 0$ ), the **increase** in the Helmholtz function of a system is equal to all the reversible work ( $-PdV + \sum XdY$ ) done **on** it. Conversely, if a machine does any reversible work at constant temperature, the Helmholtz function decreases, and the **decrease** in the Helmholtz function is equal (if the temperature is held constant) to the reversible work (of all types) done **by** the machine. It is in this sense that the Helmholtz function is called the “free energy”. It is the energy, so to speak, that is free for the performance of external reversible (i.e. useful) work.

### 12.5 Gibbs Free Energy

The *Gibbs free energy*  $G$  is defined as

$$G = H - TS \quad 12.5.1$$

or, what amounts to the same thing,

$$G = A + PV. \quad 12.5.2$$

As when we first defined enthalpy, this doesn't seem to mean much until we write it in differential form:

$$dG = dH - TdS - SdT \quad 12.5.3$$

or 
$$dG = dA + PdV + VdP. \quad 12.5.4$$

Then, either from equations 12.1.5 ( $dH = TdS + VdP + \sum XdY$ ) and 12.5.3 or from equation 12.4.3 ( $dA = -SdT - PdV + \sum XdY$ ) and 12.5.4, we obtain

$$dG = -SdT + VdP + \sum XdY. \quad 12.5.5$$

That is to say that, if the temperature and pressure are constant, the increase in the Gibbs function of a system is equal to the reversible work (other than  $PdV$  work of compression) done on it. Conversely, if the temperature and pressure are held constant, and a machine is used to do external work (which may include but is not limited to  $PdV$  work of expansion), the Gibbs function decreases by the amount of reversible (i.e. useful) work done by the machine other than the  $PdV$  work of expansion.

## 12.6 *Miscellaneous Relations, the Maxwell Relations, and the Gibbs-Helmholtz Relations*

$$dU = TdS - PdV + \sum XdY \quad 12.6.1$$

$$dH = TdS + VdP + \sum XdY \quad 12.6.2$$

$$dA = -SdT - PdV + \sum XdY \quad 12.6.3$$

$$dG = -SdT + VdP + \sum XdY \quad 12.6.4$$

If the only reversible work done on or by a system is  $PdV$  work of expansion or compression, we have the more familiar forms

$$dU = TdS - PdV \quad 12.6.5$$

$$dH = TdS + VdP \quad 12.6.6$$

$$dA = -SdT - PdV \quad 12.6.7$$

$$dG = -SdT + VdP \quad 12.6.8$$

All four thermodynamic functions are functions of state (and hence their differentials are exact differentials) and therefore

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \quad 12.6.9a,b$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial H}{\partial P}\right)_S = V \quad 12.6.10a,b$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \quad 12.6.11a,b$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V \quad 12.6.12a,b$$

Further, by equating the mixed second derivatives, we obtain the four *Maxwell Thermodynamic Relations*:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad 12.6.13$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad 12.6.14$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad 12.6.15$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad 12.6.16$$

The *Gibbs-Helmholtz Relations* are trivially found from  $A = U - TS$  and  $G = H - TS$  together with equations 12.6.11a and 12.6.12a. They are

$$U = A - T\left(\frac{\partial A}{\partial T}\right)_V \quad 12.6.17$$

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_P \quad 12.6.18$$

### 12.7 The Joule and Joule-Thomson Coefficients

In Chapter 10, we studied the Joule and Joule-Thomson experiments and we calculated the Joule and Joule-Thomson coefficients. Now that we are familiar with the Helmholtz and Gibbs functions, and, in particular, with two Maxwell relations that can be derived from them, we can obtain alternative derivations for these two coefficients. These may

be easier than the derivations we gave in Chapter 10. I am indebted to Dr Greg Trayling for the derivation of the Joule coefficient; the derivation of the Joule-Thomson coefficient follows a parallel argument.

Let us start with the *Joule coefficient*. Here we are interested in how the temperature changes with volume in an experiment in which the internal energy is constant. That is, we want to derive the Joule coefficient,  $\eta = (\partial T / \partial V)_U$ .

Now entropy is a function of state – i.e. of the intensive state variables  $P$ ,  $V$  and  $T$ . ( $V$  = molar volume.) But the intensive state variables for a particular substance are related by an *equation of state*, so we need express the entropy as a function of only *two* of  $P$ ,  $V$  or  $T$ , and, since we are seeking a relation between  $V$  and  $T$ , let us choose to express  $S$  as a function of  $V$  and  $T$ , so that

$$dS = \left( \frac{\partial S}{\partial V} \right)_T dV + \left( \frac{\partial S}{\partial T} \right)_V dT. \quad 12.7.1$$

Let us look at these three terms in turn.

First,  $dS$ . In the Joule experiment, the internal energy of the gas is constant, so that

$$TdS - PdV = 0. \quad 12.7.2$$

That is, 
$$dS = \frac{PdV}{T}. \quad 12.7.3$$

For the first term on the right hand side of equation 12.7.1, we make use of the Maxwell relation, equation 12.6.15, which we derived from the Helmholtz function:

$$\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V. \quad 12.7.4$$

For the second term on the right hand side we obtain

$$\left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial S}{\partial U} \right)_V \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V / \left( \frac{\partial U}{\partial S} \right)_V = \frac{C_V}{T}. \quad 12.7.5$$

Thus, equation 12.7.1 becomes

$$\frac{PdV}{T} = \left( \frac{\partial P}{\partial T} \right)_V dV + \frac{C_V dT}{T}. \quad 12.7.6$$

Multiply through by  $T$ , and divide by  $dV$ , taking the infinitesimal limit as  $dV \rightarrow 0$ , recalling that we are dealing with an experiment in which the internal energy is constant, and we arrive at

$$P = T \left( \frac{\partial P}{\partial T} \right)_V + C_V \left( \frac{\partial T}{\partial V} \right)_U, \quad 12.7.7$$

from which we immediately obtain

$$\left( \frac{\partial T}{\partial V} \right)_U = \frac{1}{C_V} \left[ P - T \left( \frac{\partial P}{\partial T} \right)_V \right], \quad 12.7.8$$

*quod erat demonstrandum.*

Let us now consider the *Joule-Thomson coefficient*. Here we are interested in how the temperature changes with pressure in an experiment in which the enthalpy is constant. That is, we want to derive the Joule-Thomson coefficient,  $\mu = (\partial T / \partial P)_H$ .

Now entropy is a function of state – i.e. of the intensive state variables  $P$ ,  $V$  and  $T$ . ( $V$  = molar volume.) But the intensive state variables for a particular substance are related by an *equation of state*, so we need express the entropy as a function of only *two* of  $P$ ,  $V$  or  $T$ , and, since we are seeking a relation between  $P$  and  $T$ , let us choose to express  $S$  as a function of  $P$  and  $T$ , so that

$$dS = \left( \frac{\partial S}{\partial P} \right)_T dP + \left( \frac{\partial S}{\partial T} \right)_P dT. \quad 12.7.9$$

Let us look at these three terms in turn.

First,  $dS$ . In the Joule-Thomson experiment, the enthalpy of the gas is constant, so that

$$TdS + VdP = 0. \quad 12.7.10$$

That is,

$$dS = -\frac{VdP}{T}. \quad 12.7.11$$

For the first term on the right hand side of equation 12.7.9, we make use of the Maxwell relation, equation 12.6.16, which we derived from the Gibbs function:

$$\left( \frac{\partial S}{\partial P} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_P. \quad 12.7.12$$

For the second term on the right hand side we obtain

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial H}\right)_P \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P / \left(\frac{\partial H}{\partial S}\right)_P = \frac{C_P}{T}. \quad 12.7.5$$

Thus, equation 12.7.9 becomes

$$-\frac{VdP}{T} = -\left(\frac{\partial V}{\partial T}\right)_P dP + \frac{C_P dT}{T}. \quad 12.7.14$$

Multiply through by  $T$ , and divide by  $dP$ , taking the infinitesimal limit as  $dP \rightarrow 0$ , recalling that we are dealing with an experiment in which the enthalpy is constant, and we arrive at

$$-V = -T\left(\frac{\partial V}{\partial T}\right)_P + C_P\left(\frac{\partial T}{\partial P}\right)_H, \quad 12.7.15$$

from which we immediately obtain

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} \left[ T\left(\frac{\partial V}{\partial T}\right)_P - V \right], \quad 12.7.16$$

*quod erat demonstrandum.*

## 12.8 The Thermodynamic Functions for an Ideal Gas

In this section I tabulate the changes in the thermodynamic functions for an ideal gas taken from one state to another.

**One mole of an ideal gas going isothermally and reversibly from  $P_1V_1T$  to  $P_2V_2T$  or adiabatically and reversibly from  $P_1V_1T_1$  to  $P_2V_2T_2$ .**

	Isothermal	Adiabatic
Work done <b>by</b> gas	$RT \ln(V_2/V_1)^*$	$\frac{P_1V_1 - P_2V_2}{\gamma - 1} = \frac{R(T_1 - T_2)}{\gamma - 1} = C_V(T_1 - T_2)$
$U_2 - U_1$	0	$-\frac{P_1V_1 - P_2V_2}{\gamma - 1} = -\frac{R(T_1 - T_2)}{\gamma - 1} = -C_V(T_1 - T_2)$
Heat absorbed <b>by</b> gas	$RT \ln(V_2/V_1)$	0
$S_2 - S_1$	$R \ln(V_2/V_1)$	0
$H_2 - H_1$	0	$-\frac{P_1V_1 - P_2V_2}{1 - 1/\gamma} = -\frac{R(T_1 - T_2)}{1 - 1/\gamma} = -C_P(T_1 - T_2)$
$A_2 - A_1$	$-RT \ln(V_2/V_1)$	$-\frac{R(T_1 - T_2)}{\gamma - 1} - T_2S_2 + T_1S_1$
$G_2 - G_1$	$-RT \ln(V_2/V_1)$	$-\frac{R(T_1 - T_2)}{1 - 1/\gamma} - T_2S_2 + T_1S_1$

\*Note that for isothermal processes on an ideal gas, we can write  $(V_2/V_1) = (P_1/P_2)$ .

A difficulty will be noted in the entries for the increase in the Helmholtz and Gibbs functions for an adiabatic process, in that, in order to calculate  $\Delta A$  or  $\Delta G$ , it is apparently necessary to know  $S_1$  and  $S_2$ , and not merely their difference. For the time being this is a difficulty to note on one's shirt-cuff, and perhaps return to it later.

## 12.9 The Thermodynamic Functions for Other Substances

**Calculation of the change in the thermodynamic functions of any substance going reversibly from  $P_1V_1T_1$  to  $P_2V_2T_2$ .**

The first comforting thing to note is that *SUHAG* are all state functions, and therefore the change in their values is route-independent.

*Entropy.*

Entropy is a function of state (i.e. of  $PVT$ ), but since  $PVT$  are related through the equation of state, it is necessary to specify only two of these quantities. Thus, for example if we express  $S$  as a function of  $T$  and  $P$ , infinitesimal increases in these will give rise to an infinitesimal increase in  $S$  given by

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad 12.9.1$$

Now  $\left(\frac{\partial S}{\partial T}\right)_P$  is (for a reversible process)  $\frac{C_P}{T}$  (see equation 12.7.5), and  $\left(\frac{\partial S}{\partial P}\right)_T$  is (by a Maxwell relation) equal to  $-\left(\frac{\partial V}{\partial T}\right)_P$ . If we know  $C_P$  as a function of temperature, and, if we know the equation of state, we can now calculate

$$S_2 - S_1 = \int_{T_1}^{T_2} C_P \frac{dT}{T} - \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_P dP. \quad 12.9.2$$

This will enable us to calculate the change in entropy of a substance provided that we know how the heat capacity varies with temperature and provided that we know the equation of state.

For an ideal gas  $\left(\frac{\partial V}{\partial T}\right)_P = R/P$ , and so we obtain, for an ideal gas

$$S_2 - S_1 = \int_{T_1}^{T_2} C_P \frac{dT}{T} - R \ln(P_2/P_1). \quad 12.9.3$$

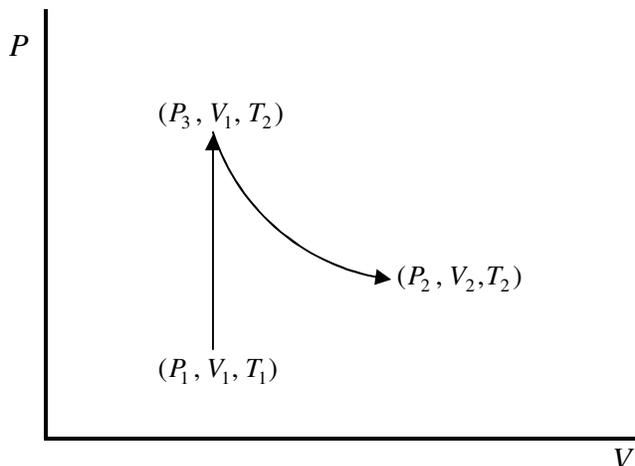
If we want to express the increase of entropy in terms of the change in temperature and volume, and of  $C_V$ , we can use  $PV = RT$  and  $C_P = C_V + R$  to obtain

$$S_2 - S_1 = \int_{T_1}^{T_2} C_V \frac{dT}{T} + R \ln(V_2/V_1). \quad 12.9.4$$

This agrees with what we had in the previous section for an isothermal expansion.

Here's another way of arriving at equation 12.9.4. We want to find the change in entropy of a mole of an ideal gas in going from  $(P_1, V_1, T_1)$  to  $(P_2, V_2, T_2)$ . Since the change in entropy is route-independent, we can choose any simple route for which the

calculation is easy. Let's go at constant volume from  $(P_1, V_1, T_1)$  to  $(P_3, V_1, T_2)$  and then at constant temperature from  $(P_3, V_1, T_2)$  to  $(P_2, V_2, T_2)$ .



To go from  $(P_1, V_1, T_1)$  to  $(P_3, V_1, T_2)$ , the gas has to absorb an amount of heat  $\int_{T_1}^{T_2} C_V dT$ , and so its entropy increases by  $\int_{T_1}^{T_2} C_V \frac{dT}{T}$ . To go from  $(P_3, V_1, T_2)$  to  $(P_2, V_2, T_2)$ . The gas does work  $RT_2 \ln(V_2/V_1)$  without any change in internal energy (because the internal energy of an ideal gas at constant temperature is independent of its volume), and therefore it absorbs this amount of heat. Therefore its entropy increases by  $R \ln(V_2/V_1)$ . Thus we arrive again at equation 12.9.4.

*Example:* If the substance is an ideal monatomic gas, then  $C_p = \frac{5}{2}R$ . From this we calculate

$$S_2 - S_1 = \frac{5}{2}R \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right) = R \ln\left[\left(\frac{T_2}{T_1}\right)^{5/2} \frac{P_1}{P_2}\right]. \quad 12.9.5$$

*Exercise:* Go through the same analysis, but starting from  $S = S(T, V)$ . Show that the result you get for an ideal gas is the same as above. It will also, of course, necessarily be the same for any substance, though the equality of the expression you get with equation 12.9.2 may not be immediately apparent.

*Exercise:* The pressure and volume of an ideal monatomic gas are both doubled. What is the ratio of the new temperature to the old? What is the increase in the molar entropy?

(I make the answer  $2.31 \times 10^4 \text{ J kmole}^{-1} \text{ K}^{-1}$ .) Now try the same problem with an ideal diatomic gas. (I make the answer  $3.46 \times 10^4 \text{ J kmole}^{-1} \text{ K}^{-1}$ .)

### *Internal Energy and Enthalpy*

These can be calculated if we know how  $C_V$  and  $C_P$  vary with temperature, because, by definition,  $C_V = (\partial U / \partial T)_V$  and  $C_P = (\partial H / \partial T)_P$ .

$$\text{Therefore} \quad U_2 - U_1 = \int_{T_1}^{T_2} C_V dT \quad 12.9.6$$

$$\text{and} \quad H_2 - H_1 = \int_{T_1}^{T_2} C_P dT. \quad 12.9.7$$

### *Helmholtz and Gibbs Functions*

Since  $A = U - TS$ , we have

$$A_2 - A_1 = U_2 - U_1 - T_2(S_2 - S_1) - S_1(T_2 - T_1). \quad 12.9.8$$

In the special case of an ideal gas, we obtain

$$A_2 - A_1 = \int_{T_1}^{T_2} C_V dT - T_2 \int_{T_1}^{T_2} \frac{C_V dT}{T} - RT_2 \ln(V_2/V_1) - S_1(T_2 - T_1). \quad 12.9.9$$

Since  $G = H - TS$ , we have

$$G_2 - G_1 = H_2 - H_1 - T_2(S_2 - S_1) - S_1(T_2 - T_1). \quad 12.9.10$$

In the special case of an ideal gas, we obtain

$$G_2 - G_1 = \int_{T_1}^{T_2} C_P dT - T_2 \int_{T_1}^{T_2} \frac{C_P dT}{T} - RT_2 \ln(P_1/P_2) - S_1(T_2 - T_1). \quad 12.9.11$$

There is, however, a serious difficulty with equations 12.9.9 and 12.9.11, in that, in order to calculate the change in the Helmholtz and Gibbs functions, we need to know the initial absolute entropy  $S_1$ .

12.10 *Absolute Entropy*

We can, of course, calculate the molar entropy of a substance at some temperature provided that we define the entropy at a temperature of absolute zero to be zero. By way of example, assuming that the molar entropy of hydrogen at 0 K is zero, calculate the absolute entropy of a kmole of H<sub>2</sub> gas at a temperature of 25°C (298.15 K) and a pressure of one atmosphere.

We can do this in five stages, as follows. You will find it helpful to sketch these stages on a drawing similar to figure VI.5.

1. Heat the solid hydrogen from 0 K to 13.95 K at a pressure of 7173 Pa. (That's the triple point.) The increase in entropy is  $\int C_p d(\ln T)$ . Assuming that we know  $C_p$  as a function of temperature in this range, that comes to 2080 J K<sup>-1</sup> kmole<sup>-1</sup>.
2. Liquefy it at the same temperature and pressure. The molar latent heat of fusion is 117000 J kmole<sup>-1</sup>. Increase in entropy = 117000/13.95 = 8400 J K<sup>-1</sup> kmole<sup>-1</sup>.
3. Vaporize it at the same temperature and pressure. The molar latent heat of vaporization is 911000 J kmole<sup>-1</sup>. Increase in entropy = 911000/13.95 = 65300 J K<sup>-1</sup> kmole<sup>-1</sup>.
4. Increase temperature to 298.15 K at constant pressure. See equation 12.9.3. The increase in entropy is  $\int C_p d(\ln T)$ . Assuming that we know  $C_p$  as a function of temperature in this range, that comes to 70000 J K<sup>-1</sup> kmole<sup>-1</sup>.
5. Increase pressure to 1 atm =  $1.013 \times 10^5$  Pa at constant temperature. See equation 12.9.4, from which we see that there is a *decrease* of entropy equal to  $R \ln(P_2/P_1) = 8314 \ln(1.013 \times 10^5 / 7173) = 22000$  J K<sup>-1</sup> kmole<sup>-1</sup>.

Hence, taking the entropy to be zero at 0 K, the required entropy is 124000 J K<sup>-1</sup> kmole<sup>-1</sup>.

Now that we have calculated the absolute entropy at a given temperature and pressure, we can calculate the increase in the Helmholtz and Gibbs functions from equations 12.9.9 and 12.9.11. But this leaves us in a rather uncomfortable position. After all, all we have done in this example is to calculate the *increase* in entropy as we took the sample up to 25 °C and 1 atmosphere – we haven't *really* calculated the *absolute* entropy. The entropy appearing in equations 12.9.9 and 12.9.11 is surely the *absolute* entropy, and we cannot calculate this unless we know the entropy at  $T = 0$  K. This slight puzzle will remain with us until Chapter 16, when we meet Nernst's Heat Theorem and the Third Law of Thermodynamics.

Many of the examples of thermodynamical calculations have hitherto involved  $PdV$  work in a system in which the working substance has been an ideal gas. Let us now look at two entirely different situations, both involving non- $PdV$  work. Let us look at charging a battery, and creating new surface by distorting a spherical drop of liquid.

### 12.11 *Charging a Battery*

The concept of “non- $PdV$  work” sometimes causes difficulty, so am going to illustrate it in this section by using the charging of a battery as an example, and in the next section by a discussion of surface tension. This section will also give us an opportunity of using a Gibbs-Helmholtz relation.

Suppose that we force a charge  $q$  into an electric cell whose electromotive force (EMF) is  $\mathcal{E}$ , at constant temperature and pressure. What is the increase in the Gibbs function of the cell? And what is the increase in its enthalpy?

The answer to the first question is easy. It is just  $q\mathcal{E}$ . The increase in the enthalpy is given by

$$\Delta H = \Delta G + T\Delta S,$$

and, by a Maxwell relation (equation 12.6.12a), this is

$$\Delta H = \Delta G - T\Delta\left(\frac{\partial G}{\partial T}\right)_p, \quad 12.11.1$$

which is one of the Gibbs-Helmholtz relations. But since  $\Delta G = q\mathcal{E}$ , this becomes

$$\Delta H = q\mathcal{E} - Tq\left(\frac{\partial \mathcal{E}}{\partial T}\right)_p = q\left[\mathcal{E} - T\left(\frac{\partial \mathcal{E}}{\partial T}\right)_p\right]. \quad 12.11.2$$

Thus we can calculate the increase in enthalpy from a measurement of how the EMF of the cell changes with temperature.

### 12.12 *Surface Energy*

For a second example of non- $PdV$  work we shall consider the phenomenon of “surface tension”.

It is well known that a liquid tends to contract to a shape that minimizes its surface area. In the absence of other forces, this means that it will become spherical. The effect is

often conveniently described in terms of “surface tension”. We describe the tendency of a surface to contract by drawing an imaginary line in the surface, and we say that the surface to one side of the line pulls the surface of the other, and we call the force per unit length perpendicular to the line the *surface tension*. It is expressed in dynes per cm or newtons per metre. In this section I shall use the following symbols:

Surface tension:  $\Gamma$   
 Area:  $\sigma$

However, from the point of view of thermodynamics, it is easier to think of surface *energy*. How much *work* is needed to increase the surface area? And how is this related to what we have described as “surface tension”? It may be noted in passing that energy per unit area ( $\text{J m}^{-2}$ ) is dimensionally similar to force per unit length ( $\text{N m}^{-1}$ ).

A non-spherical blob of liquid will, under the action of surface tension, contract into a spherical blob – i.e. a blob of least surface area for a given volume. It should not come as a surprise to learn that, at least in principle, as the blob adjusts (in an adiabatic process) to its spherical shape of least surface area, it becomes warmer. Molecules near the surface have a high potential energy. As many of them fall beneath the surface as the surface area is decreased, this potential energy is converted to kinetic energy. Conversely, if a spherical drop is distorted from its spherical shape, it becomes cooler.

We have already pointed out that the surface tension can be regarded as the work required to create new area. Increasing the area will result in a fall in temperature, so, if the temperature is kept constant, some heat must be absorbed from the surroundings, and hence the increase in the internal energy is a little more than the surface tension. It may at first seem surprising that doing work on a liquid, in order to create new surface, results in a *fall* of temperature, but the work is being used not to increase the kinetic energy of the molecules, but rather to increase their potential energy by pulling them to the surface.

One way in which we can imagine work being done on a liquid to increase its surface area is simply to imagine distorting a spherical drop into a nonspherical shape. Another way, which might lend itself more easily to the sort of thermodynamical analysis we are accustomed to in discussing gases, is to imagine a film of soapy water held in a wire frame, constructed of a fixed U-shaped portion A (see figure XII.1), and a bridge B which

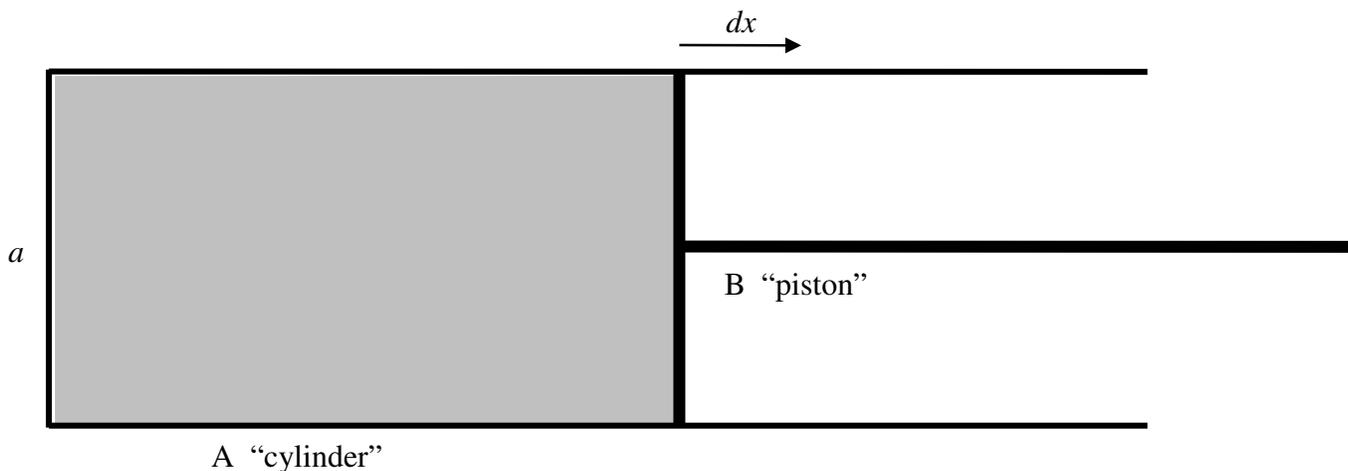


FIGURE XII.1

we can move in and out, allowing us to do work on the liquid by pulling it to the right, or the liquid to do work by pulling the bridge to the left. We could even refer to these two parts as the “cylinder” A and the “piston” B. A difference between this picture and that of a gas inside a real cylinder is that when we pull the “piston” out, we are doing work *on* the liquid. Nevertheless, as explained above, the temperature of the liquid then drops. If we allow the film to contract and to pull the “piston” to the left, the temperature will rise.

If the width of the “cylinder” is  $a$ , the surface tension force with which the liquid is pulling on the “piston” is  $2a\Gamma$ , where  $\Gamma$  is the surface tension. The factor 2 arises because there are two surfaces, above and below. If we pull the piston to the right through a distance  $dx$ , the work we do on the liquid is  $2a\Gamma dx$ . If we do this adiabatically (quickly), the liquid cools. If we do it isothermally (slowly), the liquid has to absorb some heat from its surroundings.

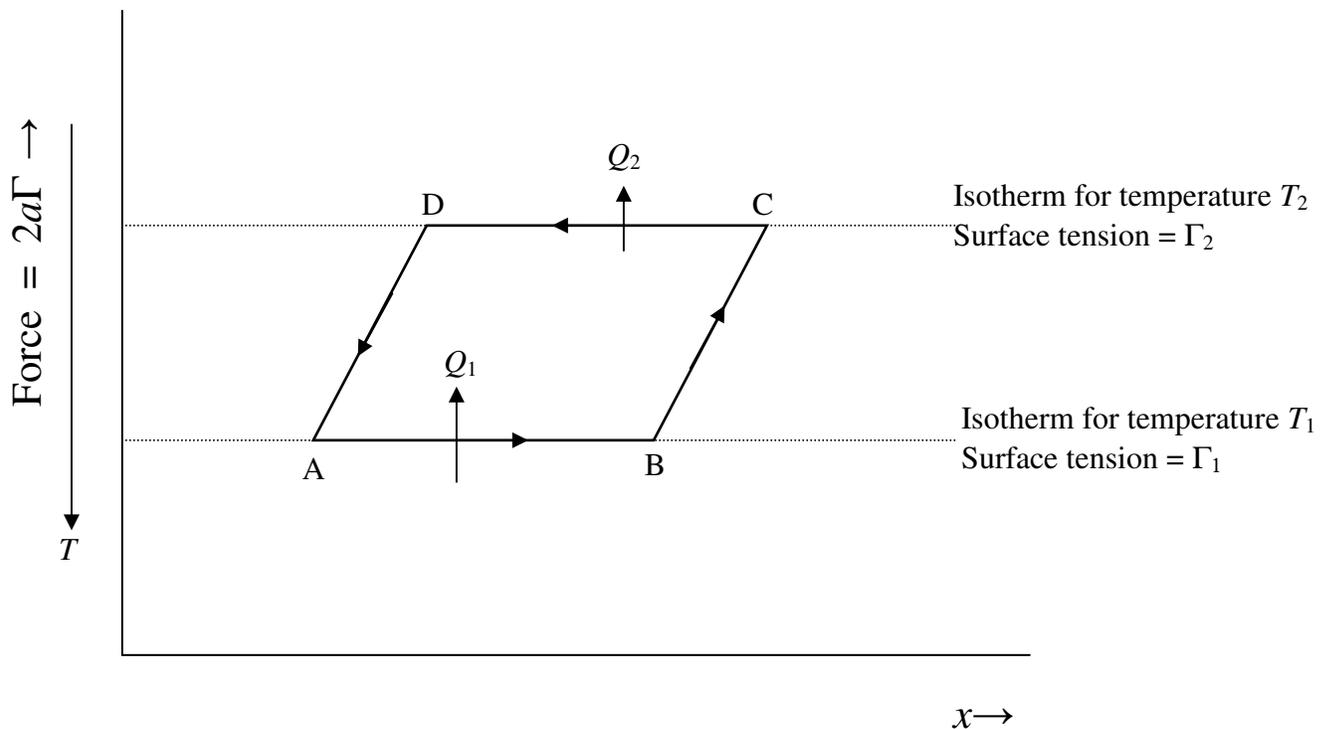


FIGURE XII.2

Let us now take the liquid around a Carnot cycle, as shown in figure XII.2. Notice that, as we move the “piston” to the right, provided that the temperature remains constant the surface tension force between the “piston” and the liquid does not change; thus the isotherms are horizontal lines, with the warmer isotherms lying lower than the cooler isotherms.

Let us start by moving the piston to the right, isothermally at a temperature  $T_1$ , through a distance  $\Delta x$ , being the portion AB of figure XII.2. The work done on the liquid is  $2a\Gamma_1\Delta x$ , where  $\Gamma_1$  is the surface tension at temperature  $T_1$ . In order that the process should be isothermal, the liquid has to absorb an amount of heat  $Q_1$  from its surroundings. The internal energy increases by  $2a\Gamma_1\Delta x + Q_1$ .

Now expand the liquid further, but this time adiabatically, from B to C. Work is being done on the liquid, but no heat is being absorbed. The temperature drops to  $T_2$ . The new surface tension is  $\Gamma_2$ , which is greater than  $\Gamma_1$ , because surface tension generally decreases at warmer temperatures.

Now allow the liquid to contract isothermally at temperature  $T_2$ , from C to D. The liquid does an amount of work  $2a\Gamma_2\Delta x$ , and it must lose an amount of heat  $Q_2$  (which, as we shall see, is less than  $Q_1$ ) to its surroundings. The internal energy decreases by  $2a\Gamma_2\Delta x + Q_2$ .

Finally, return the liquid to its original state A along the adiabatic path DA. As many molecules on the surface fall back beneath the surface, the temperature rises to its original value  $T_1$ . Work is being done *by* the liquid; the work done *by* the liquid along DA is equal to the work done *on* it along BC.

The net work done *by* the liquid around the complete cycle is  $2a(\Gamma_2 - \Gamma_1)\Delta x$ , and the net heat absorbed by the liquid around the cycle is  $Q_1 - Q_2$ . Since there is no change in the internal energy around the cycle (because  $U$  is a function of state), these two are equal. Also, there is no change in entropy around the cycle (because  $S$  is a function of state), and therefore  $Q_2/T_2 = Q_1/T_1$ . (This justifies our earlier assertion that  $Q_2 < Q_1$ .)

From these two equations we obtain

$$\frac{Q_1}{T_1}(T_1 - T_2) = 2a(\Gamma_2 - \Gamma_1)\Delta x. \quad 12.12.1$$

Go to the infinitesimal limit and drop the subscripts, and this becomes

$$Q = -T \frac{d\Gamma}{dT} \times 2a\Delta x. \quad 12.12.2$$

The right hand side is a positive quantity, because  $\frac{d\Gamma}{dT}$  is negative. We have seen that, in order to create new surface isothermally, heat must be absorbed. What equation 12.12.2 says is that the *heat absorbed* to create the new area  $\Delta\sigma = 2a\Delta x$  created is equal to

$$Q = -T \frac{d\Gamma}{dT} \times \Delta\sigma.$$

Now the *work required* to create the new area is  $\Gamma \times \Delta\sigma$ .

Thus the increase in internal energy when new area  $d\sigma$  is created at constant temperature is

$$\Delta U = \left( \Gamma - T \frac{d\Gamma}{dT} \right) \Delta\sigma. \quad 12.12.3$$

This will remind you of equation 12.11.1,  $\Delta H = \Delta G - T\Delta\left(\frac{\partial G}{\partial T}\right)_p$ , for the increase in enthalpy of a battery when we add charge to it at constant pressure. This time we are adding new area to a liquid at constant volume.

Here is *another way* at arriving at the same result: It will remind you of the way in which, in this Chapter, we derived the expression for the Joule coefficient.

The increase in internal energy and Helmholtz functions of a system when we add heat to it and do work on it is given by the familiar equations

$$dU = TdS - PdV + \sum XdY \quad 12.12.4$$

and 
$$dA = -SdT - PdV + \sum XdY. \quad 12.12.5$$

We are most familiar with them when the term  $\sum XdY$  is zero, but in this case we are dealing with a liquid at constant volume, and the one  $XdY$  term is  $\Gamma d\sigma$ , so that the equations become

$$dU = TdS + \Gamma d\sigma \quad 12.12.6$$

and 
$$dA = -SdT + \Gamma d\sigma. \quad 12.12.7$$

Divide equation 12.12.6 by  $d\sigma$  at constant temperature:

$$\left( \frac{\partial U}{\partial \sigma} \right)_T = T \left( \frac{\partial S}{\partial \sigma} \right)_T + \Gamma. \quad 12.12.8$$

From equation 12.12.7 obtain a Maxwell relation:

$$\left( \frac{\partial S}{\partial \sigma} \right)_T = - \left( \frac{\partial \Gamma}{\partial T} \right)_\sigma, \quad 12.12.9$$

except that  $\Gamma$  is in any case independent of  $\sigma$ , so the right hand term is actually a total derivative,  $d\Gamma/dT$ .

Substitute this into equation 12.12.8 and we have the same result as in our previous argument:

$$\left(\frac{\partial U}{\partial \sigma}\right)_T = \Gamma - T \frac{d\Gamma}{dT}. \quad 12.12.10$$

In summary, the increase in internal energy in creating  $d\sigma$  of new surface at constant temperature is the sum of the work required,  $\Gamma d\sigma$ , and the heat absorbed,  $-T \frac{d\Gamma}{dT} d\sigma$ .

Here's *yet another way* of getting there! It will remind you of the way in which we derived the expression for the Joule coefficient in Chapter 10. In general the internal energy of a drop of liquid depends on its volume, temperature and surface area:

$$U = U(V, T, \sigma). \quad 12.12.11$$

However, let us ignore the very small change in energy resulting from the very small amount of  $PdV$  work that the drop would do if it expands a tiny bit as a result of temperature increase. We shall be concerned only with internal energy as a function of temperature and of surface tension (which may vary with temperature.) Thus, we'll assume

$$U = U(T, \sigma). \quad 12.12.12$$

For infinitesimal increases in temperature and surface tension, the corresponding increase in the internal energy is

$$dU = \left(\frac{\partial U}{\partial T}\right)_\sigma dT + \left(\frac{\partial U}{\partial \sigma}\right)_T d\sigma. \quad 12.12.13$$

The internal energy could increase by the addition of heat **to** the drop,  $dQ$ , plus work done **on** it,  $dW$ . The former is  $TdS$ , and the latter is  $+\Gamma d\sigma$ . Thus

$$dU = TdS + \Gamma d\sigma. \quad 12.12.14$$

From these we obtain

$$dS = \frac{1}{T} \left[ \left( \frac{\partial U}{\partial T} \right)_\sigma dT + \left\{ \left( \frac{\partial U}{\partial \sigma} \right)_T - \Gamma \right\} d\sigma \right]. \quad 12.12.15$$

Since entropy is a function of state,  $dS$  is an exact differential, and therefore

$$\frac{1}{T} \frac{\partial}{\partial \sigma} \left( \frac{\partial U}{\partial T} \right)_\sigma = \frac{\partial}{\partial T} \left[ \frac{1}{T} \left( \frac{\partial U}{\partial \sigma} \right)_T - \frac{\Gamma}{T} \right]. \quad 12.12.16$$

$$\frac{1}{T} \frac{\partial^2 U}{\partial \sigma \partial T} = - \frac{1}{T^2} \left( \frac{\partial U}{\partial \sigma} \right)_T + \frac{1}{T} \frac{\partial^2 U}{\partial T \partial \sigma} + \frac{\Gamma}{T^2} - \frac{1}{T} \left( \frac{\partial \Gamma}{\partial T} \right)_\sigma. \quad 12.12.17$$

Therefore 
$$\left( \frac{\partial U}{\partial \sigma} \right)_T = \Gamma - T \left( \frac{\partial \Gamma}{\partial T} \right)_\sigma. \quad 12.12.18$$

Again, we point out that  $\Gamma$  cannot in any case depend on  $\sigma$ , so that last derivative is really a total derivative, so that

$$\left( \frac{\partial U}{\partial \sigma} \right)_T = \Gamma - T \frac{d\Gamma}{dT}. \quad 12.12.19$$

Surface tension generally decreases with temperature, so this equation shows that the increase of internal energy at constant temperature per unit new area is a little greater than the surface tension, as expected.

Can we calculate the fall in temperature if new area is created adiabatically and reversibly (i.e. isentropically)? Yes, because equation 12.12.15 (with  $dS = 0$ ) tells us that then

$$\left( \frac{\partial U}{\partial T} \right)_\sigma dT = - \left[ \left( \frac{\partial U}{\partial \sigma} \right)_T - \Gamma \right] d\sigma. \quad 12.12.20$$

On making use of equation 12.12.19, we obtain

$$\left( \frac{\partial U}{\partial T} \right)_\sigma dT = T \left( \frac{\partial \Gamma}{\partial T} \right)_\sigma d\sigma. \quad 12.12.21$$

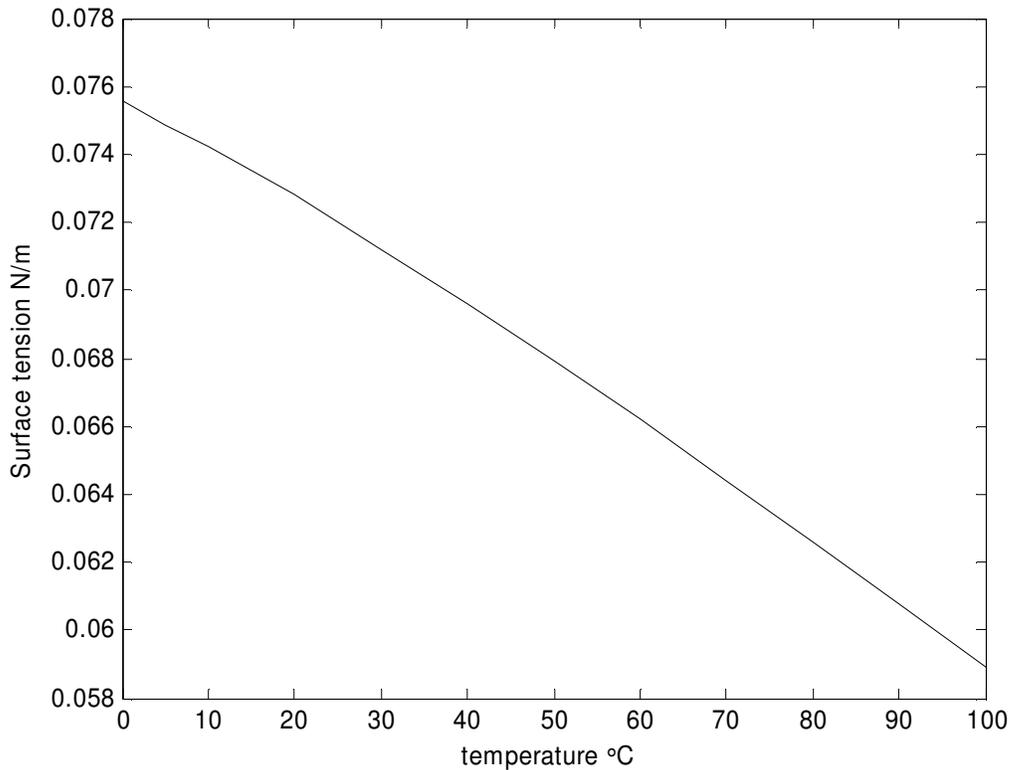
We are assuming that the volume is constant so that  $\left( \frac{\partial U}{\partial T} \right)_\sigma = C_v$ , and therefore the increase in temperature with area is

$$dT = \frac{T}{C_V} \left( \frac{\partial \Gamma}{\partial T} \right)_\sigma d\sigma = \frac{T}{C_V} \frac{d\Gamma}{dT} d\sigma. \quad 12.12.22$$

Since  $\frac{d\Gamma}{dT}$  is generally negative, this means that the temperature *falls* as the area is increased, as expected. In this equation, if  $d\sigma$  means the increase in area of a sample, in  $\text{m}^2$ , then  $C_V$  means the heat capacity of that sample, in  $\text{J K}^{-1}$ .

Measurement of the surface tension of a liquid is very sensitive to how clean the surface is, but, for the record, the following figures for the surface tension of clean water in contact with air are taken from the Website [http://www.engineeringtoolbox.com/water-surface-tension-d\\_597.html](http://www.engineeringtoolbox.com/water-surface-tension-d_597.html)

Temperature - t - (°C)	Surface Tension in contact with air - $\Gamma$ - (N/m)
0	0.0756
5	0.0749
10	0.0742
20	0.0728
30	0.0712
40	0.0696
50	0.0679
60	0.0662
70	0.0644
80	0.0626
90	0.0608
100	0.0589



*Exercise:* A drop of water 1 mm in diameter at 45 °C is broken up into two equal droplets, each half the volume of the original drop. Calculate the change in temperature, and say whether it is cooler or warmer.

### 12.13 Fugacity

*Problem:* The pressure of a mole of an ideal gas is increased isothermally from  $P_0$  to  $P$ . What is the increase  $G - G_0$  in its Gibbs free energy?

*Solution:* By integration of equation 12.6.12b,  $\left(\frac{\partial G}{\partial P}\right)_T = V$ , or by use of  $dG = -SdT + VdP$ , we have

$$G - G_0 = \int_{P_0}^P V dP. \quad 12.13.1$$

For a mole of an ideal gas,  $V = RT/P$ , and hence

$$G - G_0 = RT \ln(P/P_0), \quad 12.13.2$$

which agrees with equation 12.9.11.

Equation 12.13.1 enables us to calculate the change in the Gibbs free energy of a substance while its pressure is increased at constant temperature. Equation 12.13.2 gives the result for a mole of an ideal gas. If the substance is not an ideal gas, then we need to know the equation of state,  $V = V(P, T)$  in order to integrate equation 12.13.1. For example, the equation of state for a van der Waals gas is  $(P + a/V^2)(V - b) = RT$ , where  $V$  is the molar volume, or  $PV^3 - (bP + RT)V^2 + aV - ab = 0$ .

Integrating equation 12.13.1 with this van der Waals equation of state may appear formidable. I am grateful to Dr J. Visvanathan of Chennai, India, for pointing out that it is not necessary. Instead one can calculate the change in the Helmholtz function, which, at constant temperature, is given by  $A - A_0 = -\int_{V_0}^V PdV$ , which is easy, and then use  $G - G_0 = A - A_0 + PV - P_0V_0$ . I am also indebted to Dr Justin Albert for pointing out that this amounts to integrating  $\int_{P_0}^P VdP$  by parts, even if you had never heard of the Helmholtz function!

The *fugacity*  $f$  of a substance is defined in such a manner that, if the molar Gibbs free energy increases from  $G_0$  to  $G$ , the ratio of the new fugacity to the initial fugacity,  $f/f_0$ , is given by

$$G - G_0 = RT \ln(f / f_0). \quad 12.13.3$$

In other words, for a real substance, we can use all (or at least most!) of the equations that we know for an ideal gas as long as we substitute fugacity for pressure.

That is, 
$$f / f_0 = \exp\left(\frac{G - G_0}{RT}\right). \quad 12.13.4$$

As for internal energy, only the *difference* between the Gibbs free energies of two states can be defined; likewise, only the *ratio* of the fugacities of two states is defined.

Combining equations 12.13.4 and 12.13.1 we obtain

$$\ln(f / f_0) = \frac{1}{RT} \int_{P_0}^P VdP, \quad 12.13.5$$

which should enable us to find the relation between pressure and fugacity if we know the equation of state.

We note also that at very low pressures, a real gas behaves more and more like an ideal gas, and we can define the fugacity in units of pressure (pascal) in such a manner that, in the limit, as the pressure approaches zero, the fugacity equals the pressure. Indeed, we can then define the ratio of the fugacity to the pressure as the *activity coefficient*, which has the value unity at zero pressure.

*Problem:* Show that for a substance having the equation of state  $P(V - b) = RT$  ( $V =$  molar volume), as the pressure increases from  $P_0$  to  $P$ , the ratio of the final to initial fugacities is

$$\ln(f/f_0) = \ln(P/P_0) + \frac{b(P - P_0)}{RT}. \quad 12.13.6$$

That is, 
$$\ln f - \ln f_0 = \ln P - \ln P_0 + \frac{b(P - P_0)}{RT}. \quad 12.13.7$$

Now suppose that  $P_0$  is very small, and in the limit, as  $P_0 \rightarrow 0$ ,  $f_0 \rightarrow P_0$ . We now find that the fugacity at temperature  $T$  and pressure  $P$  is given by

$$\ln f = \ln P + \frac{bP}{RT}. \quad 12.13.8$$

This can be written

$$\frac{f}{P} = \exp\left(\frac{bP}{RT}\right). \quad 12.13.9$$

The ratio  $f/P$  is called the *activity coefficient*. You can see that  $f \approx P$  if  $P$  is small, or if  $b$  is small, as expected.