

## Chapter 16. Foundations of Thermodynamics

Given the changes in  $T$ ,  $S$ ,  $V$ ,  $P$ , and  $n_i$ , how do we calculate the corresponding change in  $U$ ,  $A$ ,  $H$ , and  $G$ ? For just one example, assume you are a diver, and that to a good degree of approximation you are essentially just a 70 kg mass of water. Calculate the change in Gibbs energy for 70 kg of water in an isothermal expansion from a pressure of 2.00 bar to a final pressure of 1.00 bar at a constant temperature of 298.2 K. This pressure difference corresponds to surfacing from a depth of 10 m.

Thermodynamics is a coherent, internally consistent, and very useful theory that allows us to predict the behavior of all macroscopic physical systems. In this chapter we find that there are amazingly few underlying principles that form the foundation for our understanding of the physical world, from a macroscopic viewpoint.

### 16.1 Thermodynamic Potentials and Thermodynamic Forces

Now that we have defined the free energy functions and determined their central importance, it is important to take a step back and consider what we have accomplished. We now have four important state functions that tell us about heat and work transfer. The internal energy is the heat transfer at constant volume, the enthalpy is the heat transfer at constant pressure, the Helmholtz energy is the maximum total work for a process, and the Gibbs energy is the maximum non-PV work for a process.  $U$ ,  $H$ ,  $A$ , and  $G$  are called thermodynamic potentials. These state functions tell us about the potential of a process to transfer heat and to do work. The idea is a generalization of the mechanical potential energy.  $U$ ,  $H$ ,  $A$ , and  $G$  tell us the potential of the system to do useful things.

There is an immediate connection between thermodynamics and classical mechanics for a process with no heat transfer. The change in thermodynamic internal energy is equal to the work done in a process when no heat is transferred,  $\Delta U = q + w = w$ . The change in mechanical potential energy,  $\mathcal{V}(x)$ , is also equal to the work done on the system; then with no heat transfer  $\Delta \mathcal{V}(x) = \Delta U = w$ . Remember from your study of classical mechanics that there is a simple relationship between the potential energy for a system and the forces that act on the system. For a particle subject to a force,  $F$ , the change in potential energy with position is:

$$F = - \frac{d\mathcal{V}(x)}{dx} \quad 16.1.1$$

The force is the negative of the gradient of the potential, Figure 16.1.1. Integrating Eq. 16.1.1 for a constant force gives the familiar relationship  $\Delta \mathcal{V}(x) = -F\Delta x$ . By analogy, we define the derivative of a thermodynamic potential against a displacement as a thermodynamic force. The displacement,  $dr$ , is a change in a thermodynamic variable, for example  $T$ ,  $S$ ,  $P$ ,  $V$ , or  $n_i$ . For the internal energy the general form of a thermodynamic force is:

$$F = \frac{\partial U}{\partial r} \quad 16.1.2$$

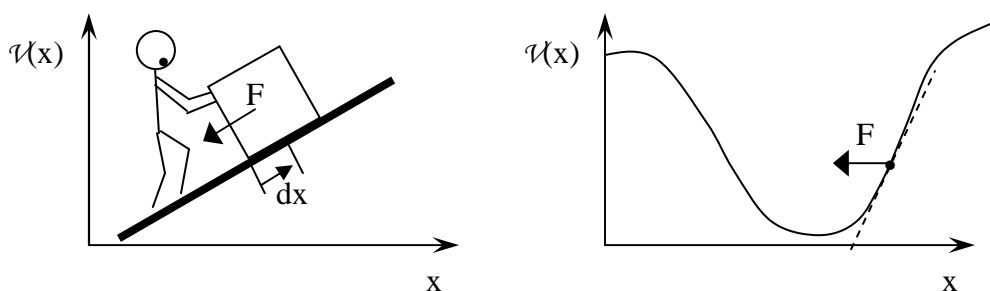


Figure 16.1.1: The change in potential energy is the work done. The work is the energy necessary to displace an object against a force. The force is the negative of the gradient of the potential.

The combined First and Second Laws of thermodynamics tell us something very important about the thermodynamic forces. For the moment, let us assume that we have a closed system with no chemical reactions, to keep things simpler. We know that the combined First and Second Laws of Thermodynamics give:

$$dU = TdS - PdV \quad (\text{closed}) \quad 16.1.3$$

which implies that the independent variables are  $S$  and  $V$ . The total differential of  $U(S, V)$  is also expressed as:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad (\text{closed}) \quad 16.1.4$$

Comparing Eq. 16.1.3 and Eq. 16.1.4 term by term gives:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \quad 16.1.5$$

These equations are in the same general form as Eq. 16.1.2, so  $T$  and  $P$  are thermodynamic forces. For  $P$  this is not at all surprising; the pressure is defined as the force per unit area. Expansion work is done against the pressure as the force. To change the volume of a system, there must be a pressure gradient. But the same arguments can be made about the temperature. Entropy change corresponds to heat flow,  $dS = dq_{\text{rev}}/T$ . To have heat flow there must be a temperature gradient. So by analogy, temperature is the force for heat flow; please review Section 13.1.

The concept of temperature is certainly one of the most fundamental principles in science. The ideal gas temperature scale is a very empirical approach to temperature, but the adoption of the ideal gas temperature scale is not a rigorous definition of temperature from a fundamental standpoint. One of the most fundamental definitions for temperature is through the thermodynamic force in Eq. 16.1.5, see Section 10.2.

The combination of  $P$  and  $V$ , couples an intensive variable and an extensive variable. The  $PV$  product gives the work done in a process and the  $PV$  product has units of energy. Variables related in this way are **conjugate variables**. The variables  $T$  and  $S$  are also a **conjugate pair**:  $T$  is the thermodynamic force that corresponds to the derivative of the potential energy with respect

to S, the product of T and S gives the heat transferred in a process, and the TS product has units of energy. The conjugate pair always occurs together in fundamental equations for the thermodynamic potentials, for example TdS and SdT. If you like, T and S go hand-in-hand, as do P and V. One variable in the pair is the force to be reckoned with while the other is the change you want to make.

The thermodynamic forces are the answers to some very important questions. For example, how does the internal energy change with volume for an adiabatic reversible process? An adiabatic reversible process corresponds to a constant entropy process. We can then just integrate the thermodynamic force:

$$\left(\frac{\partial U}{\partial V}\right)_S = -P \quad dU = -P dV \quad \text{and} \quad \Delta U = -\int PdV \quad (\text{adiabatic reversible}) \quad 16.1.6$$

How does the internal energy change with a change in entropy for a constant volume process? This problem sounds like a tough problem at first. All we need to do is to integrate our trusty thermodynamic force:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad dU = TdS \quad \text{and} \quad \Delta U = \int TdS \quad (\text{constant } V) \quad 16.1.7$$

We are on our way to being able to find the change in any thermodynamic potential with any change in variable. To make further progress we need to consider how we define the thermodynamic potentials, and why.

## 16.2 Changing Independent Variables Using Legendre Transformations

Once again consider  $dU = TdS - PdV$ . This equation gives the internal energy as a function of independent variables S and V, that is  $U(S,V)$ . S and V are the independent variables that follow from the application of the First and Second Laws, so they are called the “natural” variables of the internal energy. We have also defined:

$$H \equiv U + PV \quad 16.2.1$$

$$A \equiv U - TS \quad 16.2.2$$

$$G \equiv H - TS \quad 16.2.3$$

How do H, A, and G depend on T, S, P, and V? What are the thermodynamic forces for changes in H, A, and G?

Starting with enthalpy, the total differential is:

$$dH = dU + PdV + VdP \quad (\text{closed}) \quad 16.2.4$$

then substituting in Eq. 16.1.3 gives us:

$$dH = TdS - PdV + PdV + VdP \quad (\text{closed}) \quad 16.2.5$$

Cancelling terms gives:

$$dH = TdS + VdP \quad (\text{closed}) \quad 16.2.6$$

This equation expresses the enthalpy in terms of independent variables S and P, which are the natural variables for the enthalpy,  $H(S,P)$ , since they are directly derived from Eq. 16.1.3.

For the Helmholtz energy, the total differential is:

$$dA = dU - TdS - SdT \quad (\text{closed}) \quad 16.2.7$$

then substituting in Eq. 16.1.3 gives us:

$$dA = TdS - PdV - TdS - SdT \quad (\text{closed}) \quad 16.2.8$$

Cancelling terms gives, as we did in Eq. 15.2.10:

$$dA = - SdT - PdV \quad (\text{closed}) \quad 16.2.9$$

which corresponds to  $A(T,V)$ , with  $T$  and  $V$  the natural variables.

For Gibbs energy:

$$dG = dH - TdS - SdT \quad (\text{closed}) \quad 16.2.10$$

substituting for  $dH$  from Eq. 16.2.6 gives:

$$dG = TdS + VdP - TdS - SdT \quad (\text{closed}) \quad 16.2.11$$

and cancelling terms, as we did in Eq. 15.2.22:

$$dG = - SdT + VdP \quad (\text{closed}) \quad 16.2.12$$

The independent variables implied are  $G(T,P)$ , where  $T$  and  $P$  are the corresponding natural variables for the Gibbs energy. Notice something interesting. The natural variables for Helmholtz and Gibbs energies,  $A(T,V)$  and  $G(T,P)$ , are just those conditions where the free energy function is a good spontaneity criterion. We use  $A$  as a spontaneity criterion at constant temperature and volume, and  $G$  at constant temperature and pressure. So the choice of  $T$  and  $P$  as the independent variables makes  $G$  a good spontaneity criterion at constant  $T$  and  $P$ . This observation is another reason why we call  $T$  and  $V$  the natural variables for the Helmholtz energy, and  $T$  and  $P$  the natural variables for the Gibbs energy. But how did the natural variables for  $G$  get to be  $T$  and  $P$ ?

The natural variables for a given state function flow directly from the definition of the state function. Let's look at how we define new state functions. Let the total differential of the original state function be given as  $dF(x_1, x_2) = f_1 dx_1 + f_2 dx_2$ , with  $x_1$  and  $x_2$  as the independent variables. The definitions are all in the form:

$$Q = F - f_1 x_1 \quad 16.2.13$$

where  $Q$  is the new function and  $f_1 x_1$  is a conjugate pair of variables. This definition is called a Legendre transformation, which is widely used in many fields. Using the same steps as above, the total differential of  $Q$  is

$$dQ = dF - f_1 dx_1 - x_1 df_1 \quad 16.2.14$$

Substituting the total differential,  $dF$ ,

$$dQ = f_1 dx_1 + f_2 dx_2 - f_1 dx_1 - x_1 df_1 \quad 16.2.15$$

and cancelling terms gives;

$$dQ = - x_1 df_1 + f_2 dx_2 \quad 16.2.16$$

The net result is that the independent variables for  $Q(f_1, x_2)$  have been switched. The effect of the definition has been to switch independent variables between the  $f_1 x_1$  conjugate pair. Since one variable in a conjugate pair is intensive and the other extensive, this switch changes the independent variable from an extensive to an intensive variable or visa versa. Specifically,

starting with  $H(S,P)$ , the definition  $G \equiv H - TS$  gives the natural, independent variables  $G(T,P)$ . Why do we do this? Because, the new function,  $G$ , is the appropriate spontaneity criterion when we work at constant  $T$  and  $P$ . As we saw in the last chapter, at constant  $T$  and  $P$ , the use of Gibbs energy simplifies the system and focuses our attention on internal processes in the system, such as chemical reactions.

We now see why internal energy and enthalpy are not usually good spontaneity criteria. The natural variables for  $U$  are  $S$  and  $V$ . So internal energy is a good spontaneity criterion at constant  $S$  and  $V$ . Since adiabatic reversible processes in closed systems occur at constant entropy, there is no heat flow. As we mentioned above, with no heat flow the internal energy is equivalent to the mechanical potential energy. For example, consider the two-part system in Figure 14.3.1 where  $dU = -P_A dV_A - P_B dV_B$ . At constant entropy and total volume,  $V_{\text{tot}} = V_A + V_B$ , and  $dU = -P_A dV_A - P_B dV_B < 0$  predicts the spontaneous direction for  $PV$  work, as you used repeatedly in your work on classical mechanics. Additionally, the enthalpy is the appropriate spontaneity criterion at constant  $S$  and  $P$ .

### 16.3 Thermodynamic Forces: May the Forces Be With You

The definitions of the thermodynamic potential energy functions provide a very useful set of thermodynamic forces that provide the answers to a wide variety of problems. Starting with the natural variables for each state function,  $U(S,V)$ ,  $H(S,P)$ ,  $A(T,V)$ , and  $G(T,P)$ , the total differentials are:

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \quad dU = TdS - PdV \quad 16.3.1$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \quad dH = TdS + VdP \quad 16.3.2$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_V dT + \left(\frac{\partial A}{\partial V}\right)_T dV \quad dA = -SdT - PdV \quad 16.3.3$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \quad dG = -SdT + VdP \quad 16.3.4$$

The equations that we derived from the Legendre transforms, from Eqs. 16.2.6-16.2.12, are also listed again for convenience. Comparing terms, we can immediately write down a complete set of thermodynamic forces:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -P \quad 16.3.5$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad \left(\frac{\partial H}{\partial P}\right)_S = V \quad 16.3.6$$

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \quad \left(\frac{\partial A}{\partial V}\right)_T = -P \quad 16.3.7$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial G}{\partial P}\right)_T = V \quad 16.3.8$$

This set of forces allows us to easily solve a wide variety of problems by direct integration.

**Example 16.3.1**

Calculate the change in Helmholtz energy for one mole of an ideal gas in an isothermal expansion from an initial volume of 1 L to a final volume of 2 L at a temperature of 298.2 K.

*Answer:* Remember the trick we discussed earlier for relating partial derivatives to the conditions for a given process. The partial derivative we need gives the change in A:

$$\left(\frac{\partial A}{\partial V}\right)_T = ?$$

Let's assume for a moment that you don't recognize this particular partial derivative. How can you determine if it is a thermodynamic force? First note the numerator is the change in a potential energy function,  $dA$ . Then note that the independent variables,  $V$  and  $T$ , are the natural variables for  $A$ ; that is,  $A$  is a good spontaneity criterion at constant  $T$  and  $V$ . With the potential up top and the natural variables down below, you can recognize the derivative as the thermodynamic force for changes in  $V$ . Of course, we can just look up at the equations above and recognize that the force is  $-P$ . However, assume that you don't have Eq. 16.3.5-16.3.8 in front of you. How can you get the value for the force? Using the associations in Figure 16.3.1 we can immediately spot that  $-P$  is the force that corresponds to changes in  $A$ , with respect to changes in  $V$ . The independent variable and the force are conjugate variables.

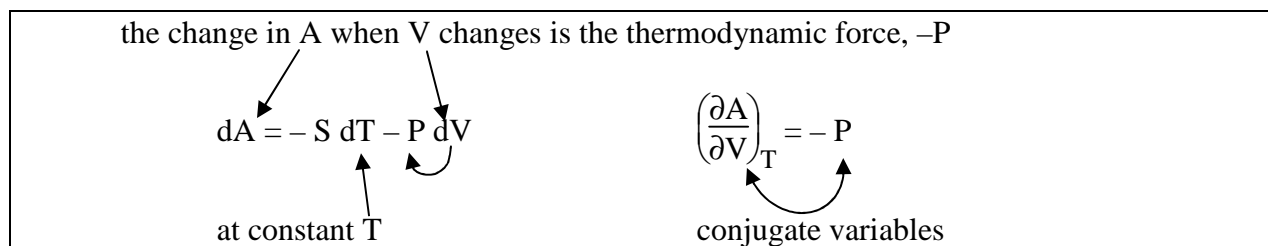


Figure 16.3.1: Finding thermodynamic forces from the total differential.

Then  $\left(\frac{\partial A}{\partial V}\right)_T = -P$  or  $dA = -P dV$

can be integrated to find the final result for an ideal gas:

$$\Delta A = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{nRT}{V} dV = - nRT \ln (V_2/V_1) \quad (\text{isothermal, ideal gas}) \quad 16.3.9^\circ$$

This result shouldn't be surprising, since  $dA = dw_{\max}$ , and the work for an isothermal reversible expansion of an ideal gas is  $w_{\text{rev}} = -nRT \ln (V_2/V_1)$ .

*The Change in Gibbs Energy with Temperature Depends on the Enthalpy Change:* The change in the Gibbs energy with temperature is given by Eq. 15.4.15. However, we can derive a simpler version of this equation based on the thermodynamic force for the change in Gibbs energy with temperature in Eq. 16.3.8. First consider the partial derivative of  $G/T$  with respect to temperature

at constant pressure. Using the product rule and Eq. 16.3.8 for the thermodynamic force  $(\partial G/\partial T)_P = -S$ , gives:

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = G\left(\frac{\partial\left(\frac{1}{T}\right)}{\partial T}\right)_P + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P = -\frac{G}{T^2} - \frac{S}{T} \quad (\text{constant P}) \quad 16.3.10$$

Then taking  $T^2$  as the common denominator gives:

$$\left(\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right)_P = -\frac{G + TS}{T^2} = -\frac{H}{T^2} \quad (\text{constant P}) \quad 16.3.11$$

where we used the definition of the Gibbs energy to find  $G + TS = H$ . This equation is called the **Gibbs-Helmholtz** equation. This result is particularly useful for chemical reactions. Remember from *General Pattern §8, Thermodynamic Relationships for Reactions*, that we can turn any thermodynamic relationship into a relationship for a chemical reaction by taking products minus reactants by inserting  $\Delta_r$ :

$$\left(\frac{\partial\left(\frac{\Delta_r G}{T}\right)}{\partial T}\right)_P = -\frac{\Delta_r H}{T^2} \quad (\text{constant P}) \quad 16.3.12$$

This result will be particularly useful when we consider the temperature dependence of equilibrium constants. Eq. 16.3.12 can be integrated by separating variables:

$$d\left(\frac{\Delta_r G}{T}\right) = -\frac{\Delta_r H}{T^2} dT \quad (\text{constant P}) \quad 16.3.13$$

and integrating from  $T_1$  to  $T_2$ :

$$\int_{\Delta_r G(T_1)/T_1}^{\Delta_r G(T_2)/T_2} d\left(\frac{\Delta_r G}{T}\right) = -\int_{T_1}^{T_2} \frac{\Delta_r H}{T^2} dT \quad (\text{constant P}) \quad 16.3.14$$

If we assume that  $\Delta_r H$  is constant over the temperature range, the integrals are:

$$\frac{\Delta_r G(T_2)}{T_2} - \frac{\Delta_r G(T_1)}{T_1} = \Delta_r H \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (\text{cst. P} \& \Delta_r H) \quad 16.3.15$$

This equation is the integrated form of the Gibbs-Helmholtz equation. This equation is also a quantitative statement of LeChâtelier's Principle for the response of a chemical reaction to changes in temperature. Consider  $T_1$  as a fixed reference temperature. For an endothermic process and an increase in temperature  $T_2$ , the right-hand side of Eq. 16.3.15 is negative. The Gibbs energy then decreases as the temperature increases as predicted by LeChâtelier's principle. Notice that the right-hand side of this equation is in the same form as discussed in *General Pattern §4*.

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### Example 16.3.2

The surfaces of nitric acid hydrates are possible catalysts that accelerate the formation of the Antarctic ozone hole. Nitric acid hydrates also act as a sink of  $\text{HNO}_3$  vapor;  $\text{HNO}_3$  vapor

photolyzes to NO and NO<sub>2</sub>, which act to slow ozone destruction. The sublimation of the trihydrate to nitric acid and water vapor:



has a  $\Delta_{\text{sub}}G^\circ$  of 93.2 kJ mol<sup>-1</sup> and a  $\Delta_{\text{sub}}H^\circ$  of 237. kJ mol<sup>-1</sup> at 220. K. The temperature in the stratosphere ranges from about 190. K to 270. K. Calculate  $\Delta_{\text{sub}}G^\circ$  at 190. K.<sup>1,2</sup>

*Answer:* Using the integrated form of the Gibbs-Helmholtz equation, assuming a constant  $\Delta_{\text{sub}}H^\circ$  over the temperature range:

$$\begin{aligned} \frac{\Delta_{\text{sub}}G^\circ(T_2)}{190. \text{ K}} - \frac{93.2 \text{ kJ mol}^{-1}}{220. \text{ K}} &= 237. \text{ kJ mol}^{-1} \left( \frac{1}{190. \text{ K}} - \frac{1}{220. \text{ K}} \right) \\ \frac{\Delta_{\text{sub}}G^\circ(T_2)}{190. \text{ K}} - 0.4236 \text{ kJ K}^{-1} \text{ mol}^{-1} &= 237. \text{ kJ mol}^{-1} (7.177 \times 10^{-4} \text{ K}^{-1}) \\ \Delta_{\text{sub}}G^\circ(190 \text{ K}) &= 112. \text{ kJ mol}^{-1} \end{aligned}$$

*The Change in Entropy with Temperature Depends on the Heat Capacity:* We used the definition of entropy directly in terms of heat transfer,  $dS = \delta q_{\text{rev}}/T$ , to derive the temperature dependence of the entropy, Eqs. 13.2.28-13.2.33. However, since entropy is a fundamental state function, it should be possible to derive the changes in entropy directly from other state functions. The thermodynamic forces allow us to do just that. Consider the change in entropy with temperature for a constant pressure process,  $(\partial S/\partial T)_P$ . The thermodynamic forces all involve a thermodynamic potential, for example  $(\partial H/\partial S)_P = T$ . We can relate the change in entropy to this thermodynamic force using the chain rule:

$$\left( \frac{\partial S}{\partial T} \right)_P = \left( \frac{\partial S}{\partial H} \right)_P \left( \frac{\partial H}{\partial T} \right)_P \quad (\text{constant P}) \quad 16.3.16$$

Inverting the thermodynamic force  $(\partial H/\partial S)_P = T$  gives:

$$\left( \frac{\partial S}{\partial H} \right)_P = \frac{1}{T} \quad (\text{constant P}) \quad 16.3.17$$

Using this thermodynamic force and the definition of  $C_p = (\partial H/\partial T)_P$  gives:

$$\left( \frac{\partial S}{\partial T} \right)_P = \frac{C_p}{T} \quad (\text{constant P}) \quad 16.3.18$$

This last equation is completely general for any system and is rigorously derived directly from the foundations of thermodynamics.

## 16.4 The Foundations of Thermodynamics

An easy way to appreciate the formalism that we are developing is to display the results in a single chart, Figure 16.4.1. We are in the middle of deriving all these relationships. The top of the chart lists the properties of the system. In thermodynamics, the system is described by an



equation of state for a gas or  $\alpha$  and  $\kappa_T$  for a liquid, solid, or solution. A heat capacity, either at constant volume or pressure is also necessary, along with a list of any chemical reactions. This top section is the only part of the chart that depends on the actual system. Everything below is perfectly general for any closed system. However, for now, to keep things simple, assume for the moment that we have a closed system with no chemical reactions. We will discuss the additions for the case when there are chemical reactions in Section 16.6.

### Foundations of Thermodynamics

$$PV = nRT \quad \alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad \frac{\alpha}{\kappa_T} = \left( \frac{\partial P}{\partial T} \right)_V$$

$$(P + a \frac{n^2}{V^2})(V - nb) = nRT \quad C_v = \left( \frac{\partial U}{\partial T} \right)_V \quad C_p = \left( \frac{\partial H}{\partial T} \right)_P$$

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$$dU = dq + dw \quad dU = TdS - PdV \quad \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V$$

$$H = U + PV \quad dH = TdS + VdP \quad \left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P$$

$$A = U - TS \quad dA = -SdT - PdV \quad \left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T$$

$$G = H - TS \quad dG = -SdT + VdP \quad \left( \frac{\partial V}{\partial T} \right)_P = - \left( \frac{\partial S}{\partial P} \right)_T$$


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$$\left( \frac{\partial U}{\partial V} \right)_T = -P + T \left( \frac{\partial P}{\partial T} \right)_V \quad C_p - C_v = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P$$

$$\left( \frac{\partial H}{\partial P} \right)_T = V - T \left( \frac{\partial V}{\partial T} \right)_P = -\mu_{JT} C_p \quad C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P = \frac{\alpha^2}{\kappa_T} VT$$

|          | <b>T</b>  | <b>V</b><br>cst. T  | <b>P</b><br>cst. T   |
|----------|---|---|--|
| <b>S</b> | $\Delta S = \int \frac{C_p}{T} dT$ @ cst.P<br>$\Delta S = C_p \ln T_2/T_1$  | $\Delta S = \int \frac{\alpha}{\kappa_T} dV$<br>$\Delta S = nR \ln V_2/V_1$ | $\Delta S = - \int \alpha V dP$<br>$\Delta S = - nR \ln P_2/P_1$ |
| <b>A</b> | $\Delta A = - \int S dT$ @ cst.V<br>$\frac{\Delta_r A_{T_2}}{T_2} - \frac{\Delta_r A_{T_1}}{T_1} = \Delta_r U \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$ | $\Delta A = - \int P dV$<br>$\Delta A = - nRT \ln V_2/V_1$                  | $\Delta A = \int PV \kappa_T dP$<br>$\Delta A = nRT \ln P_2/P_1$ |
| <b>G</b> | $\Delta G = - \int S dT$ @ cst.P<br>$\frac{\Delta_r G_{T_2}}{T_2} - \frac{\Delta_r G_{T_1}}{T_1} = \Delta_r H \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$ | $\Delta G = - \int \frac{1}{\kappa_T} dV$<br>$\Delta G = - nRT \ln V_2/V_1$ | $\Delta G = \int V dP$<br>$\Delta G = nRT \ln P_2/P_1$           |

Figure 16.4.1: Foundations of Thermodynamics.

The table at the bottom of the chart diagrams many of the possible practical problems that you might need to do. For example, the beginning example of this chapter is to calculate the change

in Gibbs energy for an isothermal change in pressure. The corresponding box in the table is in the lower right. Example 16.3.1 corresponds to the box in the middle of the table. The top result in each table cell is the general result for any system, written in terms of  $C_p$ ,  $\alpha$ , and  $\kappa_T$ . The bottom part of each cell is the result for an ideal gas. Eqs. 16.3.15 and 16.3.18 are also listed in the table.

Take a moment to find the problems in the bottom table that involve thermodynamic forces. They should be the boxes that correspond to a thermodynamic potential and its natural variables. Rather than explicitly list the thermodynamic forces in the middle section of Figure 16.4.1, we just list the definitions of the thermodynamic potentials and the corresponding total differentials in terms of the natural variables. You can use the process discussed in Exercise 16.3.1 to get the thermodynamic forces. Unfortunately, the thermodynamic forces don't solve all of our problems. To develop a perfectly general solution to any problem we need something else.....

*Maxwell Relations Simplify Relationships Involving the Entropy:* At this point we don't have a complete set of relationships that involve the entropy. These relationships are provided by Maxwell relationships. Maxwell relations are based on the fact that  $U$ ,  $H$ ,  $A$ , and  $G$  are all state functions, and therefore have exact differentials. The Euler Criterion for exactness allows us to relate derivatives of the thermodynamic forces. The Euler Criterion is that mixed partials are equal, Sec. 9.1:

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)\right)_y \quad (\text{df exact, } f \text{ a state function}) \quad 16.4.1$$

We can apply the Euler Criterion once for each thermodynamic potential.

For internal energy, the thermodynamic force for changes in entropy is the temperature, Eq. 16.3.5. In Chapter 9.8 we derived an equation for the change in temperature for an adiabatic reversible expansion for an ideal gas. Can we derive a general equation that is independent of the substance?

$$\left(\frac{\partial T}{\partial V}\right)_S = ?$$

Note that this derivative is actually a mixed partial derivative, since we can substitute Eq. 16.3.5 for  $T$ :

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)\right)_S \quad 16.4.2$$

The Euler criterion allows us to switch the order of differentiation (switch the constant variable, too).

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)\right)_V \quad 16.4.3$$

Then note from Eq. 16.3.5 that the partial derivative on the right is also a thermodynamic force,  $(\partial U/\partial V)_S = -P$ , and substitution into Eq. 16.4.3 gives:

$$\left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)\right)_V = -\left(\frac{\partial P}{\partial S}\right)_V \quad 16.4.4$$

In Figure 16.4.2 we put these steps all together so that we can see the flow of the derivation.

$$\begin{array}{c}
 dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV \\
 dU = T dS - P dV \\
 \begin{array}{cc}
 \swarrow \text{Thermodynamic force} & \searrow \text{Thermodynamic force} \\
 \left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S & = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right)_V = -\left(\frac{\partial P}{\partial S}\right)_V \\
 \uparrow \text{switch order} & \\
 \left(\frac{\partial T}{\partial V}\right)_S & = -\left(\frac{\partial P}{\partial S}\right)_V
 \end{array}
 \end{array}$$

Figure 16.4.2: Maxwell Relationship based on the internal energy. The independent variables switch and the thermodynamic forces switch.

The Maxwell relationship for the enthalpy starts with  $dH = TdS + VdP$  and  $T$  as the thermodynamic force with respect to changes in  $S$ :

$$\left(\frac{\partial H}{\partial S}\right)_P = T \quad 16.4.5$$

Form the mixed partial derivative by choosing the other independent variable,  $P$ , and switch the order of differentiation:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S\right)_P = \left(\frac{\partial V}{\partial S}\right)_P \quad 16.4.6$$

We will leave the derivation of the Maxwell relationship that comes from the Helmholtz energy as a problem at the end of the chapter. The Maxwell relationship from the Gibbs energy with  $dG = -SdT + VdP$  is particularly useful. Starting with  $-S$  as the thermodynamic force:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right)_T = -\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right)_P = -\left(\frac{\partial V}{\partial T}\right)_P \quad 16.4.7$$

Gathering together all the Maxwell relationships we find:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \quad 16.4.8$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad 16.4.9$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad 16.4.10$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad 16.4.11$$

Notice the simple pattern for the variables. We didn't derive Eq. 16.4.10, but even so it is easy to fill in from the pattern established by the other relationships: thermodynamic forces on top,

differentials for the natural variables on the bottom, with conjugate pairs of variables on the diagonals. These relationships are very powerful and will save us a lot of steps in future derivations. However, since they do seem so abstract, we will need to take extra care to show you that they are beneficial and insightful.

---

**Example 16.4.1:** Calculate  $\Delta S$  for a change in volume at constant temperature for an ideal gas.

*Answer:* The Maxwell relationship that answers this question is:

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

Substitution of the equation of state for the ideal gas,  $P = nRT/V$  gives:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial nRT/V}{\partial T}\right)_V = \frac{nR}{V}$$

Multiplication of both sides of the equation by  $dV$  gives:

$$dS = \frac{nR}{V} dV$$

This equation integrates to  $\Delta S = nR \ln \frac{V_2}{V_1}$

which we derived earlier, Eq. 13.2.4°. Of course, this equation is specific to an ideal gas. This equation is listed in the table in Figure 16.4.1.

---

**Example 16.4.2:** Calculate  $\Delta S$  for a change in volume at constant temperature for a liquid or a solid.

*Answer:* Using the same Maxwell relationship as Example 16.4.1 and Eq. 7.6.21 for the mechanical derivative gives:

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

and multiplying by  $dV$ :  $dS = \frac{\alpha}{\kappa_T} dV$

and integrating:  $\Delta S = \int \frac{\alpha}{\kappa_T} dV$

If  $\alpha$  and  $\kappa_T$  are essentially constant over the volume range:  $\Delta S = \frac{\alpha}{\kappa} \Delta V$

The problem for an ideal gas was solved in Eq. 13.2.4° without the Maxwell relations, however, this problem shows how the Maxwell relations allow us to work with real systems in a very general way.

---

The Maxwell relationships are particularly useful for solving problems involving the entropy. In particular, Eq. 16.4.10 and 16.4.11 recast a derivative involving the entropy into a derivative involving only the equation of state of the gas or  $\alpha$  and  $\kappa_T$ , as shown in the Examples. The Maxwell relationships provide quite surprising results that turn out to be very useful. In fact, this is the strength of thermodynamics: uncovering non-obvious results that are at the same time perfectly general in scope. Let's do some more examples to show the uses of the Maxwell relationships.

### 16.5 Thermodynamic Equations of State

Two partial derivatives have given us some trouble for several chapters now. We wrote the total differentials of the internal energy and the enthalpy as:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \quad 16.5.1$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \quad 16.5.2$$

We had a hard time finding general relationships for the derivatives:

$$\left(\frac{\partial U}{\partial V}\right)_T = ? \quad \left(\frac{\partial H}{\partial P}\right)_T = ?$$

Now we can see why we had troubles. The natural variables for U are S and V, while the independent variables in Eq. 16.5.1 are instead T and V. The natural variables for H are S and P, while the independent variables in Eq. 16.5.2 are T and P. Lets see if we can find general relationships using the natural variables. For the internal energy derivative,  $(\partial U/\partial V)_T$ , the variable that is held constant, T, is the “misplaced variable”. Reviewing the partial derivative conversions in Figure 9.7.2, the conversion from T as the constant variable to S is through the total differential of U. The total differential for the internal energy, assumed a function of S and V, is from Eq. 16.1.3:

$$dU = TdS - PdV \quad 16.5.3$$

Now “divide” both sides of the equation by dV at constant T to give:

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T \quad 16.5.4$$

The last partial derivative is one, but can we simplify the entropy derivative? The Maxwell relationships come to the rescue. In particular using Eq. 16.4.10 (the one you are deriving in your homework):

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \quad 16.5.5$$

This equation is called a **thermodynamic equation of state**, because all the variables on the right are related to the equation of state for the substance (who would have guessed?). This equation will help us answer some long standing questions. For an ideal gas,  $P = nRT/V$  and

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V} \quad 16.5.6^\circ$$

and substitution into Eq. 16.5.5 gives:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + \frac{nRT}{V} = -P + P = 0 \quad 16.5.7^\circ$$

We guessed this result earlier from experimental information, but now we have a rigorous derivation of the fact that the internal pressure of an ideal gas is zero. The internal energy for an ideal gas is only a function of temperature. For a liquid or solid the mechanical derivative in Eq. 16.5.5 is  $\alpha/\kappa_T$ , Eq. 7.6.16:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T \frac{\alpha}{\kappa_T} \quad 16.5.8$$

which is a general result for any system.

Now for the enthalpy derivative,  $(\partial H/\partial P)_T$ , using the total differential for the enthalpy from Eq. 16.3.2:

$$dH = TdS + VdP \quad 16.5.9$$

Dividing by  $dP$  at constant  $T$  gives:

$$\left(\frac{\partial H}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T + V \left(\frac{\partial P}{\partial P}\right)_T \quad 16.5.10$$

and using the Maxwell relationship Eq. 16.4.11:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P \quad 16.5.11$$

This equation is also called a thermodynamic equation of state. The mechanical derivative is just  $V\alpha$ :

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T V\alpha \quad 16.5.12$$

Remember that we saw in Chapter 9 that this enthalpy derivative is experimentally determined using the Joule-Thomson coefficient:

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P = -\mu_{JT} C_p \quad 16.5.13$$

which provides a nice connection to the laboratory and really ties up some loose ends from previous chapters.

One remaining loose end is the relationship between  $C_p$  and  $C_v$ . We showed that, Eq. 9.4.7:

$$C_p - C_v = \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] \left(\frac{\partial V}{\partial T}\right)_P \quad 16.5.14$$

Substituting the thermodynamic equation of state for the internal energy derivative, Eq. 16.5.5:

$$C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P = \frac{\alpha^2}{\kappa_T} VT \quad 16.5.15$$

Once again this result is completely general. The difference between  $C_p$  and  $C_v$  is given entirely in terms of the equation of state of the substance.

---

### Example 16.5.1

Calculate the change in enthalpy for one mole of liquid water for an isothermal change in pressure from 1.0 bar to 10.0 bar at 298.2 K. Assume the volume and  $\alpha$  are approximately constant over this pressure range.

*Answer:* Integrating Eq 16.5.12 assuming  $V \approx V_o$  and constant  $\alpha$  gives:

$$\Delta H = V_o \Delta P - TV_o \alpha \Delta P$$

The pure molar volume for water is  $(1.00 \text{ mol})(18.02 \text{ g mol}^{-1})/0.99705 \text{ g mL}^{-1} = 18.07 \text{ mL} = 18.07 \times 10^{-6} \text{ m}^3$ . From Table 7.6.1,  $\alpha = 2.57 \times 10^{-4} \text{ K}^{-1}$ , and  $\Delta P = (10.0 - 1.0 \text{ bar}) = 9.0 \times 10^5 \text{ Pa}$ , then:

$$\begin{aligned} \Delta H &= (18.07 \times 10^{-6} \text{ m}^3)(9.0 \times 10^5 \text{ Pa}) - 298.2 \text{ K} (18.07 \times 10^{-6} \text{ m}^3)(2.57 \times 10^{-4} \text{ K}^{-1})(9.0 \times 10^5 \text{ Pa}) \\ \Delta H &= 16.3 \text{ J} - 1.2 \text{ J} = 15.1 \text{ J} \end{aligned}$$

In other words, compared to the enthalpy of formation of water, this pressure effect is negligible.

---

### Example 16.5.2:

Show that  $C_p - C_v = nR$  for an ideal gas.

*Answer:* We will use Eq. 16.5.15, so we need to use the ideal gas law,  $P = nRT/V$  and  $V = nRT/P$  to find:

$$\begin{aligned} \left( \frac{\partial P}{\partial T} \right)_V &= \frac{nR}{V} \quad \text{and} \quad \left( \frac{\partial V}{\partial T} \right)_P = \frac{nR}{P} \\ C_p - C_v &= T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P = T \frac{nR}{V} \frac{nR}{P} \end{aligned}$$

but the first two factors combine to give  $P$ :

$$C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P = P \frac{nR}{P} = nR$$

---

## 16.6 Open Systems, Chemical Reactions, and Chemical Potential

The expressions in Figure 16.4.1 are for closed systems with no chemical reactions. For open systems we just need to add the chemical potential terms, Eq. 14.1.4:

$$dU = TdS - PdV + \sum_{i=1}^c \mu_i dn_i \quad (\text{PV \& chemical work}) \quad 16.6.1$$

For closed systems with chemical reactions, we can either specify that the  $dn_i$  are dependent variables or use Eq. 14.3.9:

$$dU = TdS - PdV + \sum_{i=1}^{n_s} \nu_i \mu_i d\xi \quad (\text{closed, PV \& chemical work}) \quad 16.6.2$$

The differentials for H, A, and G similarly add the chemical potential sum; for example for Gibbs energy, from Eq. 15.2.22:

$$dG = -SdT + VdP + \sum_{i=1}^c \mu_i dn_i \quad (\text{PV \& chemical work}) \quad 16.6.3$$

Other than these additions, no changes in Figure 16.4.1 are necessary for the thermodynamic forces involving T, S, V, and P and the Maxwell relationships, except that we need to specify constant mole amounts for the partial derivatives. For one example, Eq. 16.4.11 becomes:

$$\left(\frac{\partial S}{\partial P}\right)_{T, n_i} = -\left(\frac{\partial V}{\partial T}\right)_{P, n_i} \quad 16.6.4$$

So, we don't really need a separate figure for open systems or for chemical reactions. You can just add the chemical potential sum when you need to; thus making a much simpler figure to read. However, these results do tell us something very important about the chemical potential.

To make things simpler for a moment, assume a constant temperature and pressure process for a two component system containing components A and B. For  $dG$  from Eq. 16.6.3:

$$dG = \mu_A dn_A + \mu_B dn_B \quad (\text{cst. T\&P, chemical work}) \quad 16.6.5$$

We can also express the total differential for G at constant temperature and pressure as:

$$dG = \left(\frac{\partial G}{\partial n_A}\right)_{P, T, n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{P, T, n_A} dn_B \quad (\text{cst. T\&P, chemical work}) \quad 16.6.6$$

Comparing Eq. 16.6.6 with Eq. 16.6.5 gives the chemical potentials as:

$$\mu_A = \left(\frac{\partial G}{\partial n_A}\right)_{P, T, n_B} \quad \mu_B = \left(\frac{\partial G}{\partial n_B}\right)_{P, T, n_A} \quad 16.6.7$$

Notice that these equations are in the general form of thermodynamic forces. The chemical potential is the thermodynamic force for the change in amounts of the components. The chemical potential is the driving force for chemical change, which is just what we proved in Eq. 15.2.24. The change in the Gibbs energy is the non-PV work available from a process, and chemical change requires chemical work. The chemical potential is central to our understanding of spontaneity and equilibrium, and will be our primary tool in the next several chapters.

We should also consider the general case for multiple components. Taking G as a function of T, P, and all the  $n_i$  gives the general form of the total differential as:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T, n_i} dP + \sum_{i=1}^c \left(\frac{\partial G}{\partial n_i}\right)_{P, T, n_{j \neq i}} dn_i \quad 16.6.8$$

Comparison of terms shows with Eq. 16.6.3 that



$$\left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j \neq i}} = \mu_i \quad 16.6.9$$

for each chemical component in an open system or each constituent in a closed system with chemical reactions. The set of total differentials for the state functions then become, using Eq. 15.2.10 and Eq. 15.2.22:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_{i=1}^c \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j \neq i}} dn_i \quad dU = TdS - PdV + \sum_{i=1}^c \mu_i dn_i \quad 16.6.10$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,n_i} dS + \left(\frac{\partial H}{\partial P}\right)_{S,n_i} dP + \sum_{i=1}^c \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j \neq i}} dn_i \quad dH = TdS + VdP + \sum_{i=1}^c \mu_i dn_i \quad 16.6.11$$

$$dA = \left(\frac{\partial A}{\partial T}\right)_{V,n_i} dT + \left(\frac{\partial A}{\partial V}\right)_{T,n_i} dV + \sum_{i=1}^c \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j \neq i}} dn_i \quad dA = -SdT - PdV + \sum_{i=1}^c \mu_i dn_i \quad 16.6.12$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \sum_{i=1}^c \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j \neq i}} dn_i \quad dG = -SdT + VdP + \sum_{i=1}^c \mu_i dn_i \quad 16.6.13$$

The differentials on the right-side of Eq. 16.6.10-16.6.13 were all derived from the combined First and Second Laws of thermodynamics through Legendre transformations. Comparisons of the coefficients for the  $dn_i$  terms for the left and right-side equations show that all the chemical potential terms are equal:

$$\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j \neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j \neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j \neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j \neq i}} = \mu_i \quad 16.6.14$$

In other words, when natural variables are used, the changes in the thermodynamic potentials with changes in mole amounts are all equal. This is a wonderful result, since it would be very complicated to keep track of all the different chemical potentials, otherwise. Don't let the notational complexity of Eqs. 16.6.10-14 put you off. Just remember that the Gibbs energy change for a constant temperature and pressure process for a two component system from Eq. 16.6.13 reduces to  $dG = \mu_A dn_A + \mu_B dn_B$ .

You might wonder if we need to add additional entries to Figure 16.4.1 to express the derivatives of the chemical potential. For example, how does the chemical potential change with temperature and pressure? These derivatives can be readily obtained from the thermodynamic forces with an additional set of Maxwell relationships. For the pressure dependence:

$$\left(\frac{\partial \mu_A}{\partial P}\right)_{T,n_A,n_B} = \left(\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B}\right)_{T,n_A,n_B} = \left(\frac{\partial}{\partial n_A} \left(\frac{\partial G}{\partial P}\right)_{T,n_A,n_B}\right)_{T,P,n_B} = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} \quad 16.6.15$$

For a component in solution, the partial derivative of  $V$  is the partial molar volume,  $\bar{V}_A$ . We will discuss partial molar properties in detail in the chapter on solutions. For a pure substance, the volume derivative is just the pure molar volume of the substance,  $V_A^*$ :

$$\left(\frac{\partial\mu_A}{\partial P}\right)_{T,n_A,n_B} = \bar{V}_A \quad (\text{solution}) \qquad \left(\frac{\partial\mu_A}{\partial P}\right)_{T,n_A,n_B} = V_A^* \quad (\text{pure}) \qquad 16.6.16$$

The \* superscript is used to designate a pure substance. In other words, we simply convert the thermodynamic force  $(\partial G/\partial P)_T = V$  to a per mole basis. Consequently, we don't need to include these additional relationships in our summary table. Similarly for the change in chemical potential with temperature:

$$\left(\frac{\partial\mu_A}{\partial T}\right)_{P,n_A,n_B} = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial n_A}\right)_{T,P,n_B}\right)_{P,n_A,n_B} = \left(\frac{\partial}{\partial n_A}\left(\frac{\partial G}{\partial T}\right)_{P,n_A,n_B}\right)_{T,P,n_B} = -\left(\frac{\partial S}{\partial n_A}\right)_{T,P,n_B} \qquad 16.6.17$$

For a component in solution, the partial derivative of  $S$  is the partial molar entropy,  $\bar{S}_A$ . For a pure substance, the entropy derivative is just the pure molar entropy of the substance:

$$\left(\frac{\partial\mu_A}{\partial T}\right)_{P,n_A,n_B} = \bar{S}_A \quad (\text{solution}) \qquad \left(\frac{\partial\mu_A}{\partial T}\right)_{P,n_A,n_B} = -S_A^* \quad (\text{pure}) \qquad 16.6.18$$

One particularly important application of Eq. 16.4.16 is the calculation of the chemical potential for a pure substance as a function of the pressure for an isothermal process in a closed system. Integrating Eq. 16.6.16 from the standard state pressure,  $P^\circ$ , and standard state chemical potential,  $\mu_A^\circ(g)$ , to a final pressure  $P$  gives:

$$\mu_A - \mu_A^\circ(g) = \int_{P^\circ}^P V_A^* dP \qquad (\text{closed, cst. } T, \text{ pure}) \qquad 16.6.19$$

Assuming the gas behaves as an ideal gas,  $V_A^* = RT/P$ , the integral is:

$$\mu_A = \mu_A^\circ(g) + RT \ln P/P^\circ \qquad (\text{closed, cst. } T, \text{ pure}) \qquad 16.6.20^\circ$$

In other words, the chemical potential of an ideal gas increases as the pressure increases; the gas is able to do more useful work. The pressure dependence of the chemical potential is the foundation for the theories of phase transitions, solutions, and chemical equilibria. However, Eq. 16.6.20° only applies to ideal gases. How do we calculate the chemical potential of a real gas as a function of pressure?

## 16.7 Fugacity is the Chemically Effective Pressure

The pressure of an ideal gas depends only on the number of molecules in the system and is independent of the identity of the molecules,  $P = nRT/V$ . A mole of ideal benzene vapor is equivalent to a mole of ideal helium. The pressure of a real gas depends on intermolecular forces. The chemical potential is the available chemical work per mole for the system, which also depends strongly on intermolecular forces. The functional form of Eq. 16.6.20°, on the other hand, is particularly simple. G. N. Lewis had a particularly useful and clever idea. It would be most convenient to have the functional form of the chemical potential for a real gas be in the same form as the chemical potential of an ideal gas. By doing so, the functional form of any equation that we derive for an ideal gas will also apply to a real gas. To accomplish this simplification, Lewis defined the **fugacity**,  $f$ , as the “chemically effective” pressure. The fugacity is defined by the same functional form as Eq. 16.6.20°:

$$\mu_A = \mu_A^\circ(g) + RT \ln f/P^\circ \qquad 16.7.1$$

where  $f$  is the required value to give the exact chemical potential for the substance. The fugacity has units of pressure and takes into account the intermolecular forces as well as the number of molecules in the system. For the fugacity to be a useful concept, we also require that the fugacity approach the pressure in the ideal gas limit,  $f \rightarrow P$  as  $P \rightarrow 0$ . The “chemically effective” pressure should approach the measured pressure as the gas becomes ideal, and intermolecular forces become insignificant. To calculate the fugacity, we begin again with Eq. 16.6.19, for an isothermal process in a closed system.

Consider the system at two different pressures  $P$  and  $P'$ . The difference in chemical potential for an ideal gas is given by Eq. 16.6.20° evaluated at  $P$  and  $P'$ :

$$\begin{aligned}\mu_A^{\text{id}}(P) - \mu_A^{\text{id}}(P') &= [\mu_A^\circ(\text{g}) + RT \ln P/P^\circ] - [\mu_A^\circ(\text{g}) + RT \ln P'/P^\circ] \\ \mu_A^{\text{id}}(P) - \mu_A^{\text{id}}(P') &= RT \ln P/P'\end{aligned}\quad (\text{cst. T, ideal}) \quad 16.7.2^\circ$$

where we use the superscript “id” to remind us that the chemical potentials are for an ideal gas. Alternatively, the difference in chemical potential is also given by the integral in Eq. 16.6.19 from  $P'$  to  $P$ :

$$\mu_A^{\text{id}}(P) - \mu_A^{\text{id}}(P') = RT \ln P/P' = \int_{P'}^P V_A^{\text{id}} dP \quad (\text{cst. T, ideal}) \quad 16.7.3^\circ$$

For a real gas, we substitute the fugacity for the pressure in the logarithmic term and the volume is the real molar volume of the gas,  $V_A$ :

$$\mu_A(P) - \mu_A(P') = RT \ln f/f' = \int_{P'}^P V_A dP \quad (\text{cst. T}) \quad 16.7.4$$

We can compare the fugacity to the pressure by subtracting Eq. 16.7.3° from Eq. 16.7.4:

$$RT \ln f/f' - RT \ln P/P' = \int_{P'}^P V_A dP - \int_{P'}^P V_A^{\text{id}} dP = \int_{P'}^P (V_A - V_A^{\text{id}}) dP \quad (\text{cst. T}) \quad 16.7.5$$

This expression can be simplified by assuming that the lower limit  $P'$  is sufficiently low that the gas behaves ideally,  $P' \rightarrow 0$  then  $f' \rightarrow P'$ , giving:

$$RT \ln f/P' - RT \ln P/P' = \int_{P'}^P (V_A - V_A^{\text{id}}) dP \quad (P' \rightarrow 0, \text{cst. T}) \quad 16.7.6$$

$$RT \ln f/P = \int_0^P (V_A - V_A^{\text{id}}) dP \quad (\text{cst. T}) \quad 16.7.7$$

This last equation allows the fugacity to be calculated from the equation of state of the gas, Eq. 7.5.5, Figure 16.7.1a:

$$V_A = z RT/P \quad \text{and} \quad V_A^{\text{id}} = RT/P \quad 16.7.8$$

where the compressibility factor can be determined directly by experiment or expressed by the Virial expansion, Eq. 7.5.10. Substituting the real and ideal equations of state into Eq. 16.7.7 gives a simple prescription for calculating the fugacity of a substance:

$$\ln f/P = \int_0^P \frac{(z-1)}{P} dP \quad (\text{cst. T}) \quad 16.7.9$$

This last equation can also be rewritten noting that  $d \ln P = dP/P$  to give:

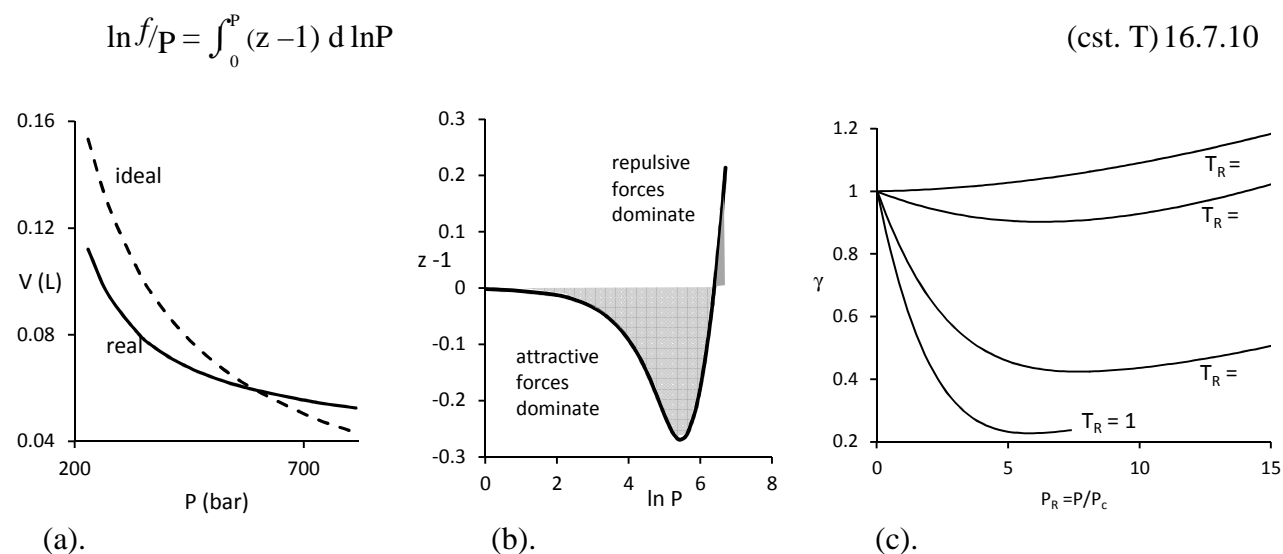


Figure 16.7.1: (a). Equations of state for the real gas as compared to an ideal gas determine the fugacity. (b). The fugacity is a function of the integrated non-ideality of the gas starting at  $P = 0$ . (c). The Law of Corresponding States allows the estimation of the fugacity coefficient from the reduced temperature and pressure (see the Appendix Data Section for a larger plot).

Data must be available over the pressure range from zero up to the pressure of interest. The fugacity is a function of the integrated non-ideality of the gas starting at  $P = 0$ , Figure 16.7.1b. Since the fugacity is the “chemically effective” pressure, we can focus on the difference between the fugacity and the pressure by defining the fugacity coefficient,  $\gamma$ , using the expression:

$$f \equiv \gamma P \quad 16.7.11$$

At low pressures the gas approaches ideal behavior giving  $\gamma = 1$ ; the fugacity is equal to the pressure. At moderate pressures, attractive forces dominate giving  $\gamma < 1$ . At high pressures, the molecules are very close together and repulsive forces dominate giving  $\gamma > 1$ . Extensive tabulations of fugacity coefficients are available. However, for most purposes we can take advantage of the Law of Corresponding states to provide an adequate estimate for  $\gamma$ .

When expressed as a function of the reduced variables, all gases follow the same equation of state, to a good approximation. Using the compressibility factor data from Figure 7.5.4, the integral in Eq. 16.7.10 can be done numerically to find good estimates for the fugacity coefficient as a function of the reduced temperature and pressure, Figure 16.7.1c (and the Appendix Data Section). Geologists, chemical engineers, and oceanographers need to use fugacities to solve practical problems, since they often work at high pressures.

#### Example 16.7.1: Calculating fugacity

Carbon dioxide sequestration has been suggested as a method to decrease  $\text{CO}_2$  release into the atmosphere from fossil fuel combustion.  $\text{CO}_2$  at high pressure is absorbed by a variety of solid or liquid sorbents. Calculate the chemical potential of  $\text{CO}_2$  at 150 bar, relative to the standard state chemical potential, at the critical temperature, 304.14 K. Use Figure 16.7.1 in the Data Section.

*Answer:* The critical pressure is 73.84 bar, Table 7.5.2. The given pressure corresponds to a reduced pressure of  $P_R = 150 \text{ bar}/73.84 \text{ bar} = 2.03$ . Using Figure 16.7.1, the fugacity coefficient is approximately  $\gamma = 0.44$ . The chemical potential using Eqs. 16.7.1 and  $f \equiv \gamma P$ , Eq. 16.7.11, is:

$$\begin{aligned}\mu_A &= \mu_A^\circ(\text{g}) + RT \ln f/P^\circ \\ &= \mu_A^\circ(\text{g}) + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} (304.1 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln[0.44(150 \text{ bar})/1 \text{ bar}] \\ &= \mu_A^\circ(\text{g}) + 10.6 \text{ kJ mol}^{-1}\end{aligned}$$

The chemical potential difference assuming ideal behavior,  $\gamma = 1$ , is  $12.7 \text{ kJ mol}^{-1}$ . Assuming ideal behavior results in a 20% error.

## 16.8 Gibbs Energy of Mixing

A good way to get used to chemical potentials is to calculate the Gibbs energy for a simple process. Consider preparing a mixture of two gases or a solution from  $n_A$  moles of pure component A and  $n_B$  moles of pure component B. As mentioned above, the chemical potential of a pure substance is just the Gibbs energy per mole:

$$\mu_i^* = \left( \frac{\partial G_i^*}{\partial n_i} \right)_{P, T, n_{j \neq i}} \quad \text{and} \quad G_i^* = \int_0^{n_i} \mu_i^* dn_i = \mu_i^* n_i \quad (\text{pure substance}) \quad 16.8.1$$

The left-hand side of the integrated form can be written as just  $G_i^*$  because the integral is from 0 to  $n_i$  moles and the Gibbs energy at the lower endpoint is zero for zero moles. Integrating Eq. 16.6.5, the Gibbs energy before mixing,  $G_1$ , is then:

$$dG = \mu_A^* dn_A + \mu_B^* dn_B \quad G_1 = \mu_A^* n_A + \mu_B^* n_B \quad (\text{cst. T\&P}) \quad 16.8.2$$

The chemical potentials vary with pressure or concentration. However, the general idea of the Gibbs energy per mole is still a useful way to think about the chemical potential in mixtures. In Chapter 18 we show how to determine chemical potentials in solution. Keeping this pressure and concentration dependence in mind, we need to integrate Eq. 16.6.5 for the formation of the mixture.

We can't integrate  $dG = \mu_A dn_A + \mu_B dn_B$  directly, if we don't know how the chemical potentials vary. However, we can use a very useful trick, **integration at constant composition**. Consider the process in Figure 16.8.1 where the two components of the mixture are added to a beaker simultaneously.

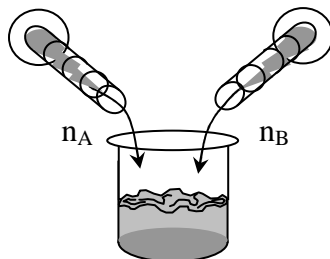


Figure 16.8.1: Integration at constant composition. Since each drop of solution formed always has the same concentration, the chemical potentials of the components are constant.

If we add the components so that the composition of the mixture is always the same as the final composition, the chemical potentials of the two components will remain constant as we mix. (Neat trick!). The integrals:

$$G_2 = \int_0^{n_A} \mu_A \, dn_A + \int_0^{n_B} \mu_B \, dn_B \quad (\text{cst. T\&P}) \quad 16.8.3$$

are now very easy to do, because the chemical potentials for each component are constants. The integrals then give the Gibbs energy for the mixture,  $G_2$ , as:

$$G_2 = \mu_A n_A + \mu_B n_B \quad (\text{cst. T\&P}) \quad 16.8.4$$

The change in Gibbs energy for mixing, using Eqs. 16.8.4 and 16.8.2, is:

$$\Delta_{\text{mix}}G = G_2 - G_1 = \mu_A n_A + \mu_B n_B - (\mu_A^* n_A + \mu_B^* n_B) \quad (\text{cst. T\&P}) \quad 16.8.5$$

$$\Delta_{\text{mix}}G = n_A(\mu_A - \mu_A^*) + n_B(\mu_B - \mu_B^*) \quad (\text{cst. T\&P}) \quad 16.8.6$$

In this equation,  $\mu_A - \mu_A^*$  is the difference in chemical potential between the mixture and the pure substance for component A. This equation is the foundation for understanding solutions. However, for now, consider the mixing of two ideal gases as an example.

*The Mixing of Ideal Gases is Always Spontaneous:* Consider a divided container with  $n_A$  moles of ideal gas A and  $n_B$  moles of ideal gas B, at the same temperature and pressure. The total moles of gas is  $n_{\text{tot}} = n_A + n_B$ . After the divider is removed, the gases mix to give mole fractions  $y_A = n_A/n_{\text{tot}}$  and  $y_B = n_B/n_{\text{tot}}$  at the same temperature and pressure, Figure 16.8.2a.

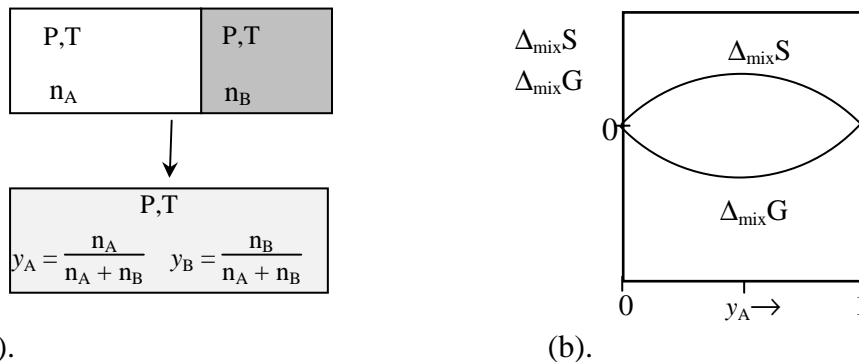


Figure 16.8.2: (a). Mixing of ideal gases at constant temperature and pressure is always spontaneous. (b). For mixing of ideal gases,  $\Delta_{\text{mix}}H = 0$ , so that  $\Delta_{\text{mix}}G = -T \Delta_{\text{mix}}S$ .

The chemical potentials of pure A and B before mixing are given by Eq. 16.6.20°:

$$\mu_A^* = \mu_A^\circ(\text{g}) + RT \ln \frac{P}{P^\circ} \quad \text{and} \quad \mu_B^* = \mu_B^\circ(\text{g}) + RT \ln \frac{P}{P^\circ} \quad (\text{cst. T\&P}) \quad 16.8.7^\circ$$

The chemical potentials of A and B after mixing are given by the partial pressures,  $P_A$  and  $P_B$ :

$$\mu_A = \mu_A^\circ(\text{g}) + RT \ln \frac{P_A}{P^\circ} \quad \text{and} \quad \mu_B = \mu_B^\circ(\text{g}) + RT \ln \frac{P_B}{P^\circ} \quad (\text{cst. T\&P}) \quad 16.8.8^\circ$$

We can compare the chemical potentials in the mixture to the pure chemical potentials by subtracting Eqs. 16.8.7° from Eqs. 16.8.8°:

$$\mu_A - \mu_A^* = RT \ln \frac{P_A}{P^\circ} - RT \ln \frac{P}{P^\circ} \quad \text{giving:} \quad \mu_A = \mu_A^* + RT \ln \frac{P_A}{P}$$

and

$$\mu_B - \mu_B^* = RT \ln \frac{P_B}{P^\circ} - RT \ln \frac{P}{P^\circ} \quad \text{giving:} \quad \mu_B = \mu_B^* + RT \ln \frac{P_B}{P} \quad (\text{cst. T\&P}) \quad 16.8.9^\circ$$

The partial pressures in the gas mixture are given from the mole fractions using Dalton's Law of Partial Pressures, Eq. 2.1.10°. Substituting  $P_A = y_A P$ , and  $P_B = y_B P$  in to Eqs. 16.8.9° gives:

$$\mu_A = \mu_A^* + RT \ln y_A \quad \text{and} \quad \mu_B = \mu_B^* + RT \ln y_B \quad (\text{cst. T\&P}) \quad 16.8.10^\circ$$

The Gibbs energy of mixing is then obtained by substituting these last equations into Eq. 16.8.6 and cancelling the terms for the pure chemical potentials,  $\mu_A^*$  and  $\mu_B^*$ :

$$\Delta_{\text{mix}}G = n_A RT \ln y_A + n_B RT \ln y_B \quad (\text{cst. T\&P}) \quad 16.8.11^\circ$$

We can get better insight into the mixing process by rewriting this last expression completely in terms of the mole fractions. Multiplying and dividing each term by  $n_{\text{tot}}$  and factoring out the resulting common factor of  $n_{\text{tot}}RT$  gives:

$$\Delta_{\text{mix}}G = n_{\text{tot}}RT \left( \frac{n_A}{n_{\text{tot}}} \ln y_A + \frac{n_B}{n_{\text{tot}}} \ln y_B \right) \quad (\text{cst. T\&P}) \quad 16.8.12^\circ$$

$$\Delta_{\text{mix}}G = n_{\text{tot}}RT (y_A \ln y_A + y_B \ln y_B) \quad (\text{cst. T\&P}) \quad 16.8.13^\circ$$

The Gibbs energy of mixing is seen to be a function only of the numbers of molecules and the temperature. This result has important implications for the entropy and enthalpy of mixing. The entropy is the thermodynamic force for the change in Gibbs energy with temperature, Eq. 16.3.8. Taking the temperature derivative of Eq. 16.8.13° and noting that the mole fractions are independent of temperature gives:

$$\Delta_{\text{mix}}S = - \left( \frac{\partial \Delta_{\text{mix}}G}{\partial T} \right)_{P, n_A, n_B} = - n_{\text{tot}}R (y_A \ln y_A + y_B \ln y_B) \quad (\text{cst. T\&P}) \quad 16.8.14^\circ$$

The change in entropy results from the increase in translational entropy as each component expands from its initial volume to the final combined volume. Energy is dispersed from the initial small volumes to the final large volume. However, the two components must, in addition, be distinguishable. A and B can't be the same substance; otherwise there is no entropy change. The requirement of distinguishability leads to the interpretation of Eq. 16.8.14° as the statistical mixing of the two gases.<sup>3</sup> (If you covered Chapter 12, note that we also derived this last equation using purely statistical arguments, Eq. 12.4.19). The enthalpy of mixing can be found using Eqs. 16.8.13°, 16.8.14°, and  $\Delta_{\text{mix}}G = \Delta_{\text{mix}}H - T \Delta_{\text{mix}}S$ :

$$\Delta_{\text{mix}}H = \Delta_{\text{mix}}G + T \Delta_{\text{mix}}S = 0 \quad (\text{cst. T\&P}) \quad 16.8.15^\circ$$

The enthalpy of mixing of ideal gases is zero, because ideal gases have no intermolecular forces. The A–A, B–B, and A–B interactions are all zero. The Gibbs energy of mixing is, then, entirely the result of the entropy of mixing:

$$\Delta_{\text{mix}}G = - T \Delta_{\text{mix}}S \quad (\text{cst. T\&P}) \quad 16.8.16^\circ$$

Since the logarithm of a number less than 1 is negative, the entropy of mixing from Eq. 16.2.14° is always positive. Then from Eq. 16.8.13°, the Gibbs energy of mixing is always negative, or spontaneous, for the mixing of two ideal gases, Figure 16.8.2b. If more than two components are mixed, Eqs. 16.8.13° and 16.8.14° are sums over each of the  $c$  components:

$$\Delta_{\text{mix}}S = -n_{\text{tot}}R \sum_{i=1}^c y_i \ln y_i \quad (\text{cst. T\&P}) \quad 16.8.17^\circ$$

$$\Delta_{\text{mix}}G = n_{\text{tot}}RT \sum_{i=1}^c y_i \ln y_i \quad (\text{cst. T\&P}) \quad 16.8.18^\circ$$

We will use these results as a foundation for understanding the mixing of components to form a solution in Chapter 18.

### 16.9 Summary–Looking Ahead

The thermodynamic potential energy functions are good spontaneity criteria for the conditions that match the natural variables. The natural variables for each potential energy function are derived from the combined First and Second Laws of thermodynamics and Legendre transformations:  $U(S,V)$ ,  $H(S,P)$ ,  $A(T,V)$ , and  $G(T,P)$ . The foundations of thermodynamics provide a prescription for calculating the changes in the thermodynamic potentials for any process and are completely general for any system. The result is a powerful, fundamental, and general method for predicting the spontaneous direction for any macroscopic process. For example, the mixing of ideal gases is always spontaneous. For ideal gases, the Gibbs energy of mixing is purely entropic. In the next chapters, we use these foundations to study phase transitions, solutions, and chemical reactions in detail. Thermodynamics is an important tool for understanding the behavior of substances in solution and the effect of solute-solvent interactions on chemical reactivity.

The generality of thermodynamics is an expression of the underlying form of nature. The essence of thermodynamics can be summarized in just one figure, Figure 16.4.1.

### Chapter Summary

1. The pairs of variables  $(P,V)$ ,  $(T,S)$ ,  $(\mu,n)$  are conjugate variables. In a conjugate pair one variable is intensive and one extensive. One is an independent variable and one is a thermodynamic force. The product of each conjugate pair has the units of energy and determines the heat or work transferred for a process.
2. The definitions of the thermodynamic potential energy functions are Legendre transformations that switch the role of the variables in the corresponding conjugate pair. For example in  $G \equiv H-TS$ , the independent variables are changed from  $H(S,P)$  to  $G(T,P)$ .
3. The natural variables for a thermodynamic potential energy function are the independent variables that result from the combined First and Second Laws of thermodynamics and the Legendre transformation specified by the definition of the function. The natural variables are the variables that must be constant for the potential energy function to be a good spontaneity criterion.



4. Maxwell relationships relate derivatives of the thermodynamic forces. Maxwell relationships are useful for simplifying problems that involve the entropy change for a process. The relationships are given by the fact that mixed partials are equal for state functions.
5. The thermodynamic forces and Maxwell relations are summarized in Figure 16.4.1.
6. The thermodynamic equations of state express changes in a thermodynamic potential energy function in terms of the equation of state of the substance:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T \left(\frac{\partial P}{\partial T}\right)_V = -P + T \frac{\alpha}{\kappa_T}$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P = V - T V \alpha$$

7. The thermodynamic equations of state allow the calculation of  $C_p - C_v$  from the equation of state of the substance:

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = \frac{\alpha^2}{\kappa_T} V T$$

8. For open systems:

$$dU = TdS - PdV + \sum_{i=1}^c \mu_i dn_i \quad dH = TdS + VdP + \sum_{i=1}^c \mu_i dn_i$$

$$dA = -SdT - PdV + \sum_{i=1}^c \mu_i dn_i \quad dG = -SdT + VdP + \sum_{i=1}^c \mu_i dn_i$$

9. For a closed system with chemical reactions:

$$dU = TdS - PdV + \sum_{i=1}^{n_s} v_i \mu_i d\xi \quad dH = TdS + VdP + \sum_{i=1}^{n_s} v_i \mu_i d\xi$$

$$dA = -SdT - PdV + \sum_{i=1}^{n_s} v_i \mu_i d\xi \quad dG = -SdT + VdP + \sum_{i=1}^{n_s} v_i \mu_i d\xi$$

10. The chemical potentials with respect to  $U$ ,  $H$ ,  $A$ , and  $G$  in terms of the corresponding set of natural variables are equivalent:

$$\left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j \neq i}} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_{j \neq i}} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j \neq i}} = \left(\frac{\partial G}{\partial n_i}\right)_{P,T,n_{j \neq i}} = \mu_i$$

11. Maxwell relationships give the thermodynamic forces for the chemical potential:

$$\left(\frac{\partial \mu_A}{\partial P}\right)_{T,n_A,n_B} = \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} \quad \text{and} \quad \left(\frac{\partial \mu_A}{\partial T}\right)_{P,n_1,n_B} = -\left(\frac{\partial S}{\partial n_A}\right)_{T,P,n_B}$$

These equations are the per mole equivalents of the thermodynamic forces in Figure 16.4.1.

12. For an isothermal change in pressure for a pure substance A:  $\mu_A - \mu_A^\circ(g) = \int_{P^\circ}^P V_A^* dP$

13. For an isothermal change in pressure for an ideal gas:  $\mu_A = \mu_A^\circ(g) + RT \ln P/P^\circ$ .

14. The fugacity is the “chemically effective” pressure, which includes the effects of intermolecular forces. The fugacity is defined to give the exact chemical potential of the gas:

$$\mu_A = \mu_A^\circ(g) + RT \ln f/P^\circ.$$

15. The fugacity coefficient is defined to focus on the deviation from ideality of the gas:  $f \equiv \gamma P$  with  $\gamma \rightarrow 1$  for  $P \rightarrow 0$ .

16. The fugacity is calculated by integrating the non-ideality of the gas from zero pressure up to

$$\text{the pressure of interest: } \ln f/P = \int_0^P (z-1) \frac{dP}{P} = \int_0^P (z-1) d \ln P$$

17. At constant temperature and pressure the Gibbs energy of mixing is

$$\Delta_{\text{mix}}G = n_A(\mu_A - \mu_A^*) + n_B(\mu_B - \mu_B^*)$$

18. The Gibbs energy of mixing for ideal gases is entirely entropic,  $\Delta_{\text{mix}}G = -T \Delta_{\text{mix}}S$ .

$$\text{At constant T and P: } \Delta_{\text{mix}}S = -n_{\text{tot}}R \sum_{i=1}^c y_i \ln y_i \quad \Delta_{\text{mix}}G = n_{\text{tot}}RT \sum_{i=1}^c y_i \ln y_i \quad \Delta_{\text{mix}}H = 0$$

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### Chapter 16: Problems

1. Assume you are a diver. To a good degree of approximation, you are essentially just a 70 kg mass of water. Calculate the change in Gibbs energy for 70.0 kg of water in an isothermal expansion from a pressure of 2.00 bar to a final pressure of 1.00 bar at a constant temperature of 298.2 K. This pressure difference corresponds to surfacing from a depth of 10 m. Start with the required partial derivative.
2. What is the thermodynamic force that corresponds to the change in Gibbs energy with temperature at constant pressure? Explain your reasoning.
3. What is the thermodynamic force that corresponds to the change in Helmholtz energy with volume at constant temperature? Explain your reasoning.
4. Calculate the change in Gibbs energy for one mole of ideal gas for a change in pressure from 1.00 bar to 2.00 bar at a constant temperature of 298.2 K. Determine the partial derivative that relates to this problem, and integrate the result (review Section 9.7).
5. Develop a problem that is based on the partial derivative  $(\partial A/\partial V)_T$ , and solve the problem (review Section 9.7). Choose an ideal gas as the system for simplicity.
6. For a given increase in volume, will diamond or liquid water give a larger increase in entropy at constant temperature?

7. Calculate the change in chemical potential for an ideal gas for a change in pressure from 1.00 bar to 20.0 bar at a constant temperature of 25°C.

8. The temperature dependence of the Gibbs energy of a chemical reaction is expressed as:

$$\frac{\Delta_r G_{T_2}}{T_2} - \frac{\Delta_r G_{T_1}}{T_1} = \Delta_r H \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

What would you plot on the axes of a graph to get a straight line with the slope related to  $\Delta_r H$ ? How is the slope related to  $\Delta_r H$ ?

9. Hydrogen is used as a fuel for internal combustion engines. However, the average combustion temperature is significantly higher than tabulated values. Calculate the standard state Gibbs energy of combustion of  $H_2$  at 700.0 K.

10. The Gibbs-Helmholtz expression, Eq. 16.3.15, gives the temperature dependence of the reaction Gibbs energy. You should remember from General Chemistry that the equilibrium constant for a chemical reaction is related to the reaction Gibbs energy by  $\Delta_r G^\circ = -RT \ln K$ . Use the Gibbs-Helmholtz equation to find the temperature dependence of the equilibrium constant.

11. Potassium hydrogen phthalate, KHP, is a commonly used primary standard for acid-base titrations. KHP is moderately soluble in water. For the reaction:  $KHP(s) \rightleftharpoons K^+(aq) + HP^-(aq)$ , the reaction Gibbs energy is given in the table, below, versus temperature at constant pressure.<sup>1</sup> Calculate the reaction enthalpy and entropy, including uncertainties. Assume the reaction enthalpy and entropy are not functions of temperature.

|                                      |       |       |       |       |        |
|--------------------------------------|-------|-------|-------|-------|--------|
| T (°C)                               | 0.6   | 22.0  | 45.0  | 55.0  | 65.0   |
| $\Delta_r G$ (kJ mol <sup>-1</sup> ) | 5.995 | 3.999 | 2.208 | 1.044 | 0.1591 |

12. Starting with the internal energy as a function of entropy and volume, give the Legendre transformation that defines a new function that will be a good spontaneity criterion at constant temperature and volume.

13. Show that  $C_v$  is not a function of volume for an ideal gas, in a closed system.

14. Calculate the change in Helmholtz energy for  $V_0$  liters of a liquid substance with isothermal compressibility  $\kappa_T$  when the pressure is changed from  $P_1$  to  $P_2$  at constant temperature. Start by proving that:

$$\left( \frac{\partial A}{\partial P} \right)_T = PV\kappa_T$$

Then integrate assuming the volume may be considered a constant  $V \approx V_0$ .

15. Derive the Maxwell relationship that is based on the Helmholtz energy:  $\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V$

16. Starting with the thermodynamic force for the change in internal energy with respect to entropy, prove that:

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

17. Show that if  $S$  is regarded as a function of  $T$  and  $V$  then, for a closed system:

$$T dS = C_v dT + T \left(\frac{\alpha}{\kappa_T}\right) dV$$

18. Show for an isothermal change in pressure for a liquid or a solid,  $\Delta S = - \int \alpha V dP$ .

19. Pressure perturbation calorimetry has become a useful tool in studies of protein folding. In interpreting the effects of solvation on protein conformation and folding, the following derivative is centrally important. Show that:

$$\left(\frac{\partial C_p}{\partial P}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

20. Show that:  $\left(\frac{\partial V}{\partial S}\right)_P = \frac{\alpha VT}{C_p}$

21. Show that:  $\left(\frac{\partial P}{\partial S}\right)_V = \frac{\alpha T}{\kappa_T C_v}$

22. Reversible adiabatic processes are constant entropy processes. Derive Eq. 9.8.12° directly from  $(\partial T/\partial V)_S$ . Do this derivation in two steps. (a). Show that:

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

(b). Integrate this last equation for an ideal gas from the initial state,  $T_1$  and  $V_1$ , to the final state,  $T_2$  and  $V_2$ .

23. Reversible adiabatic processes are constant entropy processes. Derive Eq. 9.8.18° directly from  $(\partial T/\partial P)_S$ . Do this derivation in two steps. (a). Show that:

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

(b). Integrate this last equation for an ideal gas from the initial state,  $T_1$  and  $P_1$ , to the final state,  $T_2$  and  $P_2$ .

24. The heat capacity of a substance can be determined without heat flow measurements by determining the change in temperature of a substance with pressure at constant entropy,  $(\partial T/\partial P)_S$ . Constant entropy conditions are obtained by changing the pressure rapidly, so that heat flow is minimal. Reversible adiabatic processes are constant entropy processes. Show that:<sup>2</sup>

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{T}{C_p}\right) = \frac{TV\alpha}{C_p}$$

(b). The coefficient of thermal expansion for benzene is  $1.24 \times 10^{-3} \text{ K}^{-1}$  and the density is  $0.8765 \text{ g/cm}^3$  at  $298.15 \text{ K}$ . The temperature of a sample of benzene increased by  $0.0484 \text{ K}$  for a sudden increase in pressure of  $2.02 \text{ bar}$ . Calculate the heat capacity of benzene.<sup>2</sup>

25. Consider the change in Gibbs energy for an isothermal change in pressure for a liquid or a solid. Assume the volume changes and that the isothermal compressibility,  $\kappa_T$ , is constant.

(a). Show that for initial volume  $V_o$ , initial pressure  $P_o$ , and final pressure  $P$ , for moderate changes in pressure:

$$\Delta G = V_o (P - P_o) - \frac{1}{2} V_o \kappa_T (P - P_o)^2$$

(b). Repeat Problem 1 with this more accurate formula, and compare the results.

26. (a). Calculate the change in internal energy for one mole of liquid water for an isothermal decrease in volume from  $1.0000 \text{ L}$  to  $0.9900 \text{ L}$  at  $298.2 \text{ K}$  and an initial pressure of  $1.00 \text{ bar}$ . Assume that  $\alpha$  and  $\kappa_T$  are approximately constant over this volume range. Note that to a good approximation:

$$P = P_o - \frac{1}{V_o \kappa_T} (V - V_o)$$

(b). Calculate the final pressure.

27. Calculate the change in Gibbs energy of a liquid substance with isothermal compressibility  $\kappa_T$  when the volume is changed from  $V_1$  to  $V_2$  at constant temperature. Start by proving that:

$$\left(\frac{\partial G}{\partial V}\right)_T = -\frac{1}{\kappa_T}$$

Then integrate from  $V_1$  to  $V_2$  assuming  $\kappa_T$  is constant.

28. The Gibbs-Helmholtz relationship is useful at constant pressure. Show that for constant volume processes:

$$\left(\frac{\partial \left(\frac{A}{T}\right)}{\partial T}\right)_V = -\frac{U}{T^2}$$

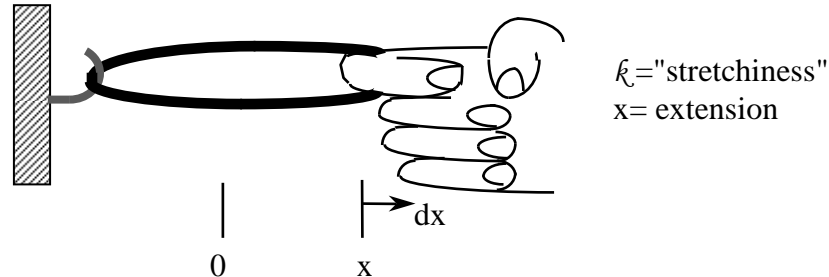
29. Rewrite Figure 9.7.1 for the partial derivatives:

$$\left(\frac{\partial G}{\partial T}\right)_V \quad \left(\frac{\partial T}{\partial G}\right)_P \quad \left(\frac{\partial G}{\partial V}\right)_T \quad \left(\frac{\partial G}{\partial T}\right)_V \quad \left(\frac{\partial P}{\partial T}\right)_G$$

30. In an isothermal expansion of an ideal gas  $\Delta U = 0$ . The value is not zero for a real gas. Using the Van der Waals equation of state, find  $\Delta U$  for an isothermal expansion from  $V_1$  to  $V_2$ .

31. The work for the system in stretching a rubber band is  $w_{\text{net}} = -F dx$ , where  $F$  is the restoring force,  $F = -\kappa x$ . At constant temperature and pressure,  $\Delta G = w_{\text{net}}$ , where  $w_{\text{net}}$  is the non-PV work. Therefore, the total change in Gibbs energy for a process involving stretching a rubber band is:

$$dG = -S dT + V dP - F dx.$$



(a). Under what conditions is  $\Delta G$  be a good spontaneity criterion (i.e. when what is held constant)? (b). For an initial state with a stretched rubber band,  $x > 0$ , find the direction for spontaneous change, either  $dx > 0$  or  $dx < 0$ , at constant temperature and pressure. (c). Define a new state function:  $R \equiv G + F x$ . What are the independent variables for  $R$ ?

32. Given that  $dU = TdS - PdV$  and for an ideal gas the change in entropy is given by:

$$dS = \frac{C_v}{T} dT + \frac{nR}{V} dV$$

show that  $dU = C_v dT$  for any process in an ideal gas. (At first it doesn't look like  $dU = TdS - PdV$  will give just  $dU = C_v dT$ , does it?)

33. In Eqs. 16.6.14, the chemical potentials expressed in terms of  $U$ ,  $H$ ,  $A$ , and  $G$  were all shown to be equal based on comparing the total differential of each thermodynamic potential with the Legendre transformed combined First and Second Laws of thermodynamics. As an alternative proof, show that the chemical potentials expressed in terms of the Gibbs energy and the enthalpy are equal using partial derivative conversions:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} = \left( \frac{\partial H}{\partial n_i} \right)_{S, P, n_{j \neq i}}$$

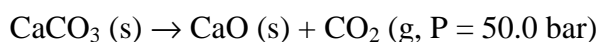
34. Calculate the entropy and Gibbs energy of mixing of 0.80 moles of  $N_2(g)$  and 0.20 moles of  $O_2(g)$  at 298.15 K. Assume the initial pure gases are at 1 bar pressure and the final total pressure is also at 1 bar.

35. Carbon sequestration is a strategy for ameliorating global climate change caused by the build-up of  $CO_2$  in the atmosphere from fossil fuel combustion. However, the separation of  $CO_2$  from exhaust gases requires work that will necessarily decrease the efficiency of the overall process. Assume that the  $O_2$  in air is replaced completely by  $CO_2$  during a combustion process. Calculate the minimum energy per mole of  $CO_2$  at constant temperature and pressure necessary to separate the  $CO_2$  from the remaining  $N_2$  at 298.15 K. Assume air is 20.9 mol%  $O_2$  and 79.1 mol%  $N_2$ . Anthracite coal can be modeled as pure graphite. Compare the energy required for the  $CO_2$  separation to the Gibbs energy of combustion of graphite.

36. Find the fugacity coefficient for a gas that obeys the Virial equation of state, Eq. 7.5.10:  $z = 1 + (B(T)/RT) P$ . For  $\text{CO}_2$  at the critical temperature, 304.14 K, the second Virial coefficient is  $B(T) = -0.114 \text{ L mol}^{-1}$ . Calculate the fugacity coefficient for  $\text{CO}_2$  at 150 bar and 304.14 K, and compare to the result using Figure 16.7.1 (see Example 16.7.1).

37. A brief outline of carbon sequestration is given in Problem 35. One proposal for carbon sequestration is to pump liquid or super critical  $\text{CO}_2$  deep underground into abandoned oil wells that are sealed by salt domes.  $\text{CO}_2$  may be liquefied at temperatures less than the critical temperature and pressures greater than the critical pressure. For  $\text{CO}_2$  the critical temperature is 304.14 K and the critical pressure is 73.843 bar. The critical pressure is the maximum vapor pressure for liquid  $\text{CO}_2$ . At equilibrium, the chemical potential of the liquid is equal to the chemical potential of the vapor,  $\mu_{\text{CO}_2}^*(\text{l}) = \mu_{\text{CO}_2}(\text{g})$ . Find the chemical potential for  $\text{CO}_2$  vapor and liquid at the critical point, relative to the standard state, using Figure 16.7.1. Compare your results to the value assuming ideal gas behavior.

38. Carbon dioxide plays an important role in many geochemical processes, which often occur at high pressure. Calculate the reaction Gibbs energy at 50.0 bar and 298.2 K for:



Approximate the fugacity coefficient using:

$$\ln \gamma \cong z - 1 \cong (B(T)/RT) P$$

where  $B(T)$  is the second Virial coefficient at the given temperature (see Problem 36 for the justification). For  $\text{CO}_2$  at 298.2 K, the second Virial coefficient is  $B(T) = -0.125 \text{ L mol}^{-1}$ . Neglect the effect of the pressure on the solids. Compare the results to the value assuming an ideal gas (Ch. 15, Problem 17).

39. (*Challenge Problem*) Consider a one-component open system:  $dU = T dS - P dV + \mu dn$ , with the chemical potential given in terms of the natural variables for  $U$  by:

$$\mu = \left( \frac{\partial U}{\partial n} \right)_{S,V}$$

For practical problems we often treat the internal energy as a function of  $T$  and  $V$ , since we often work at constant temperature and constant volume (see Chapter 7). (a). Show using partial derivative conversions that:

$$dU = T dS - P dV + \mu dn = C_v dT + \left( \frac{\partial U}{\partial V} \right)_{T,n} dV + \left( \frac{\partial U}{\partial n} \right)_{T,V} dn$$

(b). Determine  $dU$  for a constant temperature and volume process for an open system.

40. (*Challenge Problem*) The molar absolute entropies of substances that are listed in reference tables are given by:

$$S_m = \left( \frac{\partial S}{\partial n} \right)_{T,P}$$

since reference tabulations assume constant temperature and pressure. Consider a single component system. The enthalpy change for a general process in terms of the natural variables is:

$$dH = T dS + V dP + \mu dn$$

The  $TdS$  term, however, is more complicated than it might first appear. Show that:

$$T dS = C_p dT - T \left( \frac{\partial V}{\partial T} \right)_{P,n} dP + T S_m dn$$

41. (*Challenge Problem*) (a). Starting with the result for  $TdS$  from the last problem, show that for a general process in an open system with one component:

$$dH = C_p dT + \left( \frac{\partial H}{\partial P} \right)_{T,n} dP + T S_m dn + \mu dn$$

(b). The molar enthalpies for substances that are listed in reference tables are given by:

$$H_m = \left( \frac{\partial H}{\partial n} \right)_{T,P}$$

Show that  $\mu = \left( \frac{\partial H}{\partial n} \right)_{T,P} - T S_m$

(c). Combine the expressions in parts (a) and (b) and compare to the general total differential of  $H(T,P,n)$ .

(d). Find  $dH$  for a constant temperature and pressure process in an open system with one component.

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2. S. J. Gill, E. M. West, "The indirect determination of the heat capacity,  $C_p$ , of a liquid," *J. Chem. Ed.*, **1966**, *43(10)*, 557-559.