Chapter 16: Foundation of Thermodynamics 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.

Answer: The required partial derivative is $(\partial G/\partial P)_T$. This partial derivative is a thermodynamic force, $(\partial G/\partial P)_T = V$, which integrates to give $\Delta G = \int V \, dP$. This expression is given in the last column of the table in Figure 16.4.1. For small changes in pressure, we can consider $V \approx V_o$, where V_o is the initial volume. To calculate ΔG in joules, we must find V_o in m^3 and ΔP in Pa, with 1 bar = 1×10^5 Pa:

$$V_o = 70.0 \times 10^3 \text{ g}(1 \text{ mL}/0.99705 \text{ g})(1 \text{ m}^3/1 \times 10^6 \text{ mL}) = 0.07021 \text{ m}^3$$

$$\begin{aligned} \Delta G &= V_o \, \Delta P \\ &= 0.07021 \text{ m}^3 \, (1.00 \text{ bar} - 2.00 \text{ bar})(1 \times 10^5 \text{ Pa}/1 \text{ bar}) \\ &= -7021. \text{ J} = -7.02 \text{ kJ} \end{aligned}$$

Given the large amount of water representing the diver, this is a small change in Gibbs energy. The effect of small pressure changes on the Gibbs energy of a condensed phase is often less than the experimental uncertainty in the Gibbs energy. See also Chapter 15 Problem 14.

2. What is the thermodynamic force that corresponds to the change in Gibbs energy with temperature at constant pressure? Explain your reasoning.

Answer: The partial derivative that corresponds to the thermodynamic force for changes in temperature at constant pressure is:

$$\left(\frac{\partial G}{\partial T}\right)_P = ?$$

We can get this force by comparing with the total differentials for the Gibbs energy, Eq. 16.3.4:

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

Alternatively, we can use the process outlined in Figure 16.3.1:

change in G when T changes is the thermodynamic force, –S

$$dG = -\, S \, dT + V \, dP \qquad\qquad \text{giving:} \qquad\qquad \left(\frac{\partial G}{\partial T}\right)_P = -\, S$$

at constant P

<u>3</u>. What is the thermodynamic force that corresponds to the change in Helmholtz energy with volume at constant temperature? Explain your reasoning.

Answer: The partial derivative that corresponds to the thermodynamic force for changes in volume at constant temperature is:

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

We can get this force by comparing the total differentials for the Helmholtz energy, Eq. 16.3.3:

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

Alternatively, we can use the process outlined in Figure 16.3.1:

change in A   when V changes is the thermodynamic force, –P

$$dA = -\,S\,dT - P\,dV \qquad\qquad \text{giving:} \qquad \left(\frac{\partial A}{\partial V}\right)_T = -\,P$$

at constant T

<u>4</u>. 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).

Answer: The required partial derivative is $(\partial G/\partial P)_T$. This expression is given in the last column of the table in Figure 16.4.1. However, for practice, let's review the process. In $(\partial G/\partial P)_T$, the dependent variable is a thermodynamic potential. The independent variables are the natural variables for the thermodynamic potential, G(T,P). This partial derivative is then a thermodynamic force. The force is given by comparing the total differentials in general form and the form given by the Legendre transformation of the combined First and Second Laws:

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \qquad\qquad \text{giving:} \qquad \left(\frac{\partial G}{\partial P}\right)_T = V$$
$$\downarrow \qquad\qquad \downarrow$$
$$dG = -\,SdT \quad + \quad VdP$$

Integrating gives $\Delta G = \int V\, dP$. For an ideal gas V = nRT/P and:

$$\Delta G = \int nRT/P\; dP = nRT \ln P_2/P_1$$
$$= 1.00 \text{ mol}(8.3145 \text{ J K}^{-1}\text{ mol}^{-1})(298.2 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln(2.00 \text{ bar}/1.00 \text{ bar}) = 1.72 \text{ kJ}$$

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.

Answer: For one example, calculate the change in Helmholtz energy for one mole of an ideal gas for an isothermal expansion from 1.00 L to 2.00 L at 298.2 K.

   The required partial derivative is a thermodynamic force, $(\partial A/\partial V)_T = - P$, which for an ideal gas integrates to give Eq. 16.3.9° (see also Figure 16.4.1):

$$\Delta A = - nRT \ln V_2/V_1$$
$$= - 1.00 \text{ mol}(8.3145 \text{ J K}^{-1}\text{mol}^{-1})(298.2 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln(2.00 \text{ L}/1.00 \text{ L}) = -1.72 \text{ kJ}$$

6. For a given increase in volume, will diamond or liquid water give a larger increase in entropy at constant temperature?

Answer: Consulting Figure 16.4.1, note that $\Delta S = \int \alpha/\kappa_T \, dV = \alpha/\kappa_T \, \Delta V$, assuming constant α and κ_T. For diamond and liquid water, respectively, from Table 7.6.1:

diamond: $\alpha/\kappa_T = 0.030\text{x}10^{-4} \text{ K}^{-1}/0.185\text{x}10^{-6} \text{ bar}^{-1} = 16.2 \text{ bar K}^{-1}$
water: $\alpha/\kappa_T = 2.57\text{x}10^{-4} \text{ K}^{-1}/45.3\text{x}10^{-6} \text{ bar}^{-1} = 5.67 \text{ bar K}^{-1}$

Diamond will give a larger increase in entropy than water for equal changes in volume.

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.

Answer: Using Eq. 16.6.20° with the reference pressure at 1 bar, $P° = 1.00$ bar:

$$\mu_1 = \mu_1° + RT \ln \frac{P}{P°}$$

gives the change:

$$\mu_1 - \mu_1° = RT \ln \frac{P}{P°} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}(298.15 \text{ K}) \ln(20.0/1.00)$$
$$= 7.426 \text{ J K}^{-1} \text{ mol}^{-1} = 7.43 \text{ kJ mol}^{-1}$$

where the subscript for μ_1 indicates component 1. Alternatively and equivalently, for a single component you can integrate Eq. 16.6.16 directly:

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V_A^* \qquad\qquad \text{(pure substance)}$$

with $V_A^* = RT/P$ for an ideal gas:

$$\Delta\mu = \mu_2 - \mu_1 = \int_{\mu_1}^{\mu_2} d\mu = \int_{P_1}^{P_2} \frac{RT}{P} dP$$

where μ_1 is the chemical potential of the initial state and μ_2 is the chemical potential of the final state:

$$\Delta\mu = RT \ln\left(\frac{P_2}{P_1}\right)$$

This equation is analogous to Eq. 15.4.4°, $\Delta G = nRT \ln(P_2/P_1)$, for one mole of substance.

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

$$\frac{\Delta_r G_{T2}}{T_2} - \frac{\Delta_r G_{T1}}{T_1} = \Delta_r H \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

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 $\Delta_r H$?

Answer: This equation is the Gibbs-Helmholtz equation, Eq. 16.3.15. A graph of $\Delta_r G/T$ versus $1/T$ for a chemical reaction gives a straight line with slope = $\Delta_r H$, assuming the reaction enthalpy is constant over the temperature range. An endothermic reaction will give a positive slope and an exothermic reaction a negative slope.
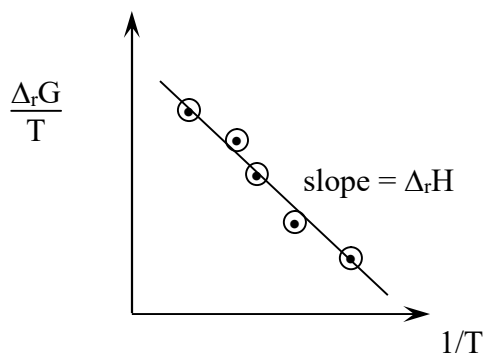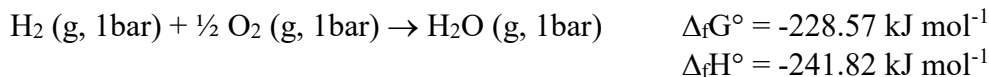

Rearranging the Gibbs-Helmholtz equation into direct straight-line form gives:

$$\frac{\Delta_r G_{T2}}{T_2} = \frac{\Delta_r H}{T_2} + \left(\frac{\Delta_r G_{T1}}{T_1} - \frac{\Delta_r H}{T_1}\right) \qquad \text{with the intercept} = \left(\frac{\Delta_r G_{T1}}{T_1} - \frac{\Delta_r H}{T_1}\right)$$

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.

Answer: The plan is to use the Gibbs-Helmholtz equation, Eq. 16.3.15, to find the reaction Gibbs energy at the higher temperature from the tabulated value at 298.2 K. The Gibbs energy of combustion of H_2 is equivalent to the Gibbs energy of formation of H_2O, which at high temperatures is water vapor.

The combustion reaction is the formation reaction, which at 298.15 K gives:

$$H_2 \text{ (g, 1bar)} + \frac{1}{2} O_2 \text{ (g, 1bar)} \rightarrow H_2O \text{ (g, 1bar)} \qquad \Delta_fG° = \text{-228.57 kJ mol}^{-1}$$
$$\Delta_fH° = \text{-241.82 kJ mol}^{-1}$$

Using the Gibbs-Helmholtz equation applied to reaction Gibbs energies, Eq. 16.3.15, gives:

$$\frac{\Delta_rG_{T2}}{T_2} - \frac{\Delta_rG_{T1}}{T_1} = \Delta_rH \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\frac{\Delta_rG_{T2}}{700.0 \text{ K}} - \frac{\text{-228.57 kJ mol}^{-1}}{298.15 \text{ K}} = \text{-241.82 kJ mol}^{-1} \left(\frac{1}{700.0 \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$\frac{\Delta_rG_{T2}}{700.0 \text{ K}} + 0.766628 \text{ kJ mol}^{-1} \text{ K}^{-1} = \text{-241.82 kJ mol}^{-1} (\text{-1.9254x10}^{-3} \text{ K}^{-1}) = 0.46561 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$\frac{\Delta_rG_{T2}}{700.0 \text{ K}} = \text{-0.30102 kJ mol}^{-1} \text{ K}^{-1}$$

$$\Delta_rG_{T2} = \text{-210.7 kJ mol}^{-1}$$

The combustion of H_2 at high temperatures provides less energy than at room temperature, as predicted by LeChâtelier's Principle and the exothermic $\Delta_rH°$. For the $(1/T_2 - 1/T_1)$ term, remember to keep at least one extra significant figure to avoid round-off error.

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 $\Delta_rG° = -RT \ln K$. Use the Gibbs-Helmholtz equation to find the temperature dependence of the equilibrium constant.

Answer: Solving $\Delta_rG° = -RT \ln K$ for $\ln K$ gives:

$$\ln K = -\Delta_rG°/RT$$

Dividing the Gibbs-Helmholtz equation by $-R$ and specifying standard state pressure gives:

$$\frac{\Delta_rG°_{T_2}}{-RT_2} - \frac{\Delta_rG°_{T_1}}{-RT_1} = \frac{\Delta_rH°}{-R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Substituting in $\ln K_{eq} = -\Delta_rG°/RT$ at both temperatures gives:

$$\ln K_{T2} - \ln K_{T1} = -\frac{\Delta_rH°}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln\left(\frac{K_{T2}}{K_{T1}}\right) = -\frac{\Delta_rH°}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where $\Delta_rH°$ is evaluated at the average temperature. This equation is found in most General Chemistry texts.

<u>11</u>. 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) $\rightleftarrows$ K$^+$ (aq) + HP$^-$ (aq), the reaction Gibbs energy is given in the table, below, versus temperature at constant pressure.[1] 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
Δ_rG (kJ mol^{-1})	5.995	3.999	2.208	1.044	0.1591

Answer: The plan is to use the thermodynamic force $(\partial\Delta_rG/\partial T)_P = -\Delta_rS$ and the Gibbs-Helmholtz expression, Eq. 16.3.15, with suitable linear plots to extract the thermodynamic parameters from the slopes.

A spreadsheet was written to plot Δ_rG versus T and also Δ_rG/T versus 1/T, as required by the Gibbs-Helmholtz expression, Eq. 16.3.15.

T (°C)	T (K)	Δ_rG (kJ mol^{-1})	1/T (K^{-1})	Δ_rG/T (J K^{-1} mol^{-1})
0.6	273.75	5.995	0.003653	218.993
22	295.15	3.999	0.003388	135.496
45	318.15	2.208	0.003143	69.402
55	328.15	1.044	0.003047	31.822
65	338.15	0.1591	0.002957	4.704

Δ_rG vs. T

slope	-0.089782	30.57353	intercept
±	0.00254	0.791182	±
r^2	0.99761	0.132461	st.dev. y
F	1249.86	3	dof
ss$_{reg}$	21.930	0.052638	ss$_{resid}$

y = -0.0898x + 30.574
R² = 0.9976

Δ_rG/T vs. 1/T

slope	30529.3	-89.63895	intercept
±	7389.73	2.39990	±
r^2	0.99825	0.417286	st.dev. y
F	1706.78	3	dof
ss$_{reg}$	297.197	0.522383	ss$_{resid}$

y = 30529x - 89.639
R² = 0.9982
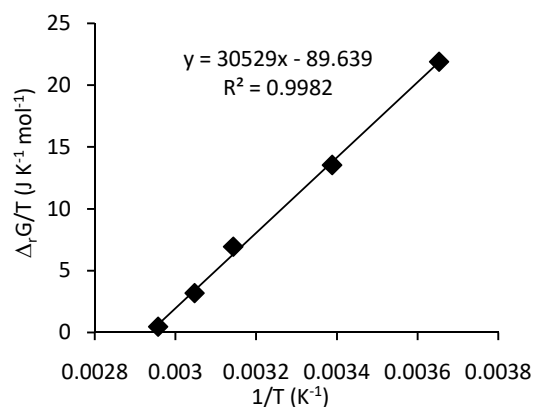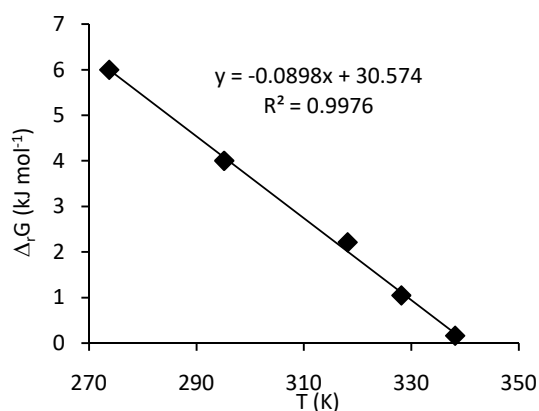
The slope of Δ_rG versus T is $-\Delta_rS$ giving: $\qquad$ $\Delta_rS = 89.8 \pm 2.5$ J K^{-1} mol^{-1}

The slope of Δ_rG/T versus 1/T gives: $\qquad$ $\Delta_rH = 30.53 \pm 0.74$ kJ mol^{-1}

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.

Answer: Consider the case with PV and chemical work. The natural variables for internal energy are S, V, and the mole amounts:

$$dU = T \, dS - P \, dV + \sum_{i=1}^{c} \mu_i \, dn_i$$

The Legendre transformation must be defined to switch the role of T and S to obtain a good spontaneity criterion at constant temperature:

$$A \equiv U - TS$$

so that dA has natural variables T and V. To show that the natural variables of the new thermodynamic potential are T, V and the mole amounts, the total differential is given by:

$$dA = dU - T \, dS - S \, dT$$

and substituting for dU gives:

$$dA = T \, dS - P \, dV + \sum_{i=1}^{c} \mu_i \, dn_i - T \, dS - S \, dT = - S \, dT - P \, dV + \sum_{i=1}^{c} \mu_i \, dn_i$$

At constant T and V the first two terms vanish giving:

$$dA = \sum_{i=1}^{c} \mu_i \, dn_i$$

which focuses our attention of the chemical work. For a spontaneous process at constant T and V, dA < 0, thus minimizing A.

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

Answer: In other words show that, for a closed system: $\left(\dfrac{\partial C_v}{\partial V}\right)_T = 0$

The definition of the constant volume heat capacity is:

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

Substitution into the partial derivative with respect to V, above, gives:

$$\left(\frac{\partial C_v}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V$$

The order of differentiation can be reversed because U is a state function, just as we did for the Maxwell relationships. For an ideal gas, $(\partial U/\partial V)_T = 0$, giving:

$$\left(\frac{\partial C_v}{\partial V}\right)_T = 0$$

In other words C_v is not a function of volume.

<u>14</u>. Calculate the change in Helmholtz energy for V_o liters of a liquid substance with isothermal compressibility κ_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 $V \approx V_o$.

Answer: Start with the desired partial derivative: $\left(\frac{\partial A}{\partial P}\right)_T = ?$

We note that the natural variables for Helmholtz energy are V and T, not the given independent variables P and T. The "misplaced variable," in the sense discussed in Section 9.7, is the derivative with respect to P in the denominator. Using the chain rule then gives:

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

The first partial derivative on the right of the equality is the thermodynamic force, Eq. 16.3.7, $(\partial A/\partial V)_T = - P$. The second partial is given from the definition of the isothermal compressibility:

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

which upon substitution gives: $\left(\frac{\partial A}{\partial P}\right)_T = \left(\frac{\partial A}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T = - P(- V\kappa_T) = PV\kappa_T$

This expression may be integrated after separating variables:

$$dA = PV\kappa_T \, dP$$

Assuming κ_T is constant and the volume change is small for moderate changes in pressure, $V \approx V_o$, gives:

$$\Delta A = \int_{P_1}^{P_2} P \, V_o \, \kappa_T \, dP = \frac{V_o \kappa_T}{2}(P_2{}^2 - P_1{}^2)$$

The Helmholtz energy for a substance increases with an increase in pressure.

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

Answer: The independent variables for this relationship are V and T. The thermodynamic potential that has natural variables V and T is the Helmholtz energy, Eq. 16.3.3. In analogy with Figure 16.4.2, the general form of the total differential and the Legendre transformed First and Second Laws are:

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

$$dA = -S\ dT - P\ dV$$

Thermodynamic force   Thermodynamic force

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

switch order

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

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

Answer: The thermodynamic force for the change in internal energy with respect to entropy is:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \qquad \text{or inverting:} \qquad \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

We can use the chain rule for the desired partial derivative with respect to temperature:

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

Using the thermodynamic force and the definition of C_v, Eq. 7.8.7, gives:

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

No approximations are made in this derivation. The equation holds for real gases, ideal gases, liquids, and solids.

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

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

10

Answer: Consider S(T,V), giving the total differential:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \qquad 1$$

We can use the chain rule for the partial derivative with respect to temperature (Problem 14):

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial U}\right)_V \left(\frac{\partial U}{\partial T}\right)_V \qquad 2$$

Notice that the thermodynamic force is:

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{or inverting:} \quad \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \qquad 3$$

Using this thermodynamic force and the definition of C_v gives:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} \qquad 4$$

Note that the partial derivative in Eq. 1 with respect to V is a Maxwell relationship, Eq. 16.4.10, which using Eq. 7.6.21 gives

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\alpha}{\kappa_T}\right) \qquad 5$$

Substituting Eqs. 4 and 5 into Eq. 1 gives:

$$dS = \frac{C_v}{T} dT + \left(\frac{\alpha}{\kappa_T}\right) dV \qquad 6$$

Finally, multiplying both sides of this last equation by T gives the final result:

$$T\, dS = C_v\, dT + T\left(\frac{\alpha}{\kappa_T}\right) dV \qquad 7$$

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

Answer: The change in entropy for a change in pressure at constant temperature is given by the partial derivative:

$$\left(\frac{\partial S}{\partial P}\right)_T = ?$$

We can recognize this partial derivative as the Maxwell Relationship that is derived from the Gibbs energy, Eq. 16.4.11, since T and P are the independent variables:

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

The right-hand side is given by the thermal expansion coefficient, Eq. 7.6.13, in the form $(\partial V/\partial T)_P = V \alpha$:

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

Separating variables and integrating gives $\Delta S = - \int \alpha V \, dP$

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:

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

Answer: Substituting from the definition of $C_p = (\partial H/\partial T)_P$ and switching the order of diffentiation:

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

We can reverse the order of differentiation, since enthalpy is a state function. Using the thermodynamic equation of state, Eq. 16.5.11, for $(\partial H/\partial P)_T$ gives:

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

Using the product rule gives the temperature derivatives as:

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

The first and the last terms on the right cancel giving the final result:

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

This equation is very useful for understanding solute-solvent interactions, because changes in volume are easy to visualize.

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

Answer: Starting with the partial derivative:

$$\left(\frac{\partial V}{\partial S}\right)_P = ? \qquad\qquad 1$$

Which variable is the "misplaced" variable in this partial derivative? Consider the definitions of α and κ_T, Eqs. 7.6.13 and 7.6.14, respectively:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{and} \quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad\qquad 2$$

These relationships suggest the "misplaced" variable in Eq. 1 is the derivative with respect to S in the denominator. Referring to Figure 9.7.2, the suggestion is to use the chain rule:

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial S}\right)_P \qquad\qquad 3$$

The first partial derivative on the right is given by the thermal expansion coefficient:

$$(\partial V/\partial T)_P = V\,\alpha \qquad\qquad 4$$

The second partial derivative in Eq. 3 can be inverted to find a more familiar form, Eq. 16.3.18:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T} \quad \text{or inverting:} \quad \left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_p} \qquad\qquad 5$$

Substituting Eqs. 4 and 5 into Eq. 3 gives the final result:

$$\left(\frac{\partial V}{\partial S}\right)_P = \frac{\alpha V T}{C_p} \qquad\qquad 6$$

This partial derivative is important because it is the result of the Maxwell relationship based on the enthalpy, Eq. 16.4.9. The Maxwell relationship and Eq. 6 allow the derivative involving the entropy to be expressed entirely in terms of a heat capacity and α.

Method 2: Like many derivations in thermodynamics, this relationship can be derived in several ways. An alternative and equivalent derivation is based on the Maxwell Relationships. Returning to Eq. 1, one quick place to look for partial derivatives involving the entropy is a Maxwell Relationship. This partial derivative is given by the Maxwell Relationship that is derived from the enthalpy, which has natural variables S and P, Eq. 16.4.9:

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S \qquad\qquad 7$$

At first this relationship doesn't look like it helps much, because we don't often work with processes at constant entropy. The "misplaced" variable is the constant entropy. We need to use the Euler chain relationship. Writing the total differential of the entropy in terms of independent variables T and P gives:

$$dS = 0 = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \qquad\qquad 8$$

Solving for $(\partial T/\partial P)_S$ gives:

$$\left(\frac{\partial T}{\partial P}\right)_S = -\frac{\left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_P}$$ 9

The partial derivative in the numerator is related through the Maxwell Relationship, Eq. 16.4.11, to the thermal expansion coefficient,

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha$$ 10

and the partial derivative in the denominator is given by Eq. 16.3.18:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$$ 11

Substituting Eqs. 9-11 into Eq. 7 gives:

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S = -\frac{(-V\alpha)}{\left(\frac{C_p}{T}\right)} = \frac{\alpha VT}{C_p}$$ 12

This equation allows the change in volume for a constant pressure process to be calculated from the change in entropy or the change in temperature for an adiabatic reversible process from the change in pressure.

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

Answer: Starting with the partial derivative:

$$\left(\frac{\partial P}{\partial S}\right)_V = ?$$ 1

Which variable is the "misplaced" variable in this partial derivative? Consider the definitions of α and κ_T, Eqs. 7.6.13 and 7.6.14, respectively and Eq. 7.6.16:

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{and} \qquad \left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\kappa_T}$$ 2

These relationships suggest the "misplaced" variable in Eq. 1 is the derivative with respect to S in the denominator. Referring to Figure 9.7.2, the suggestion is to use the chain rule:

$$\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial S}\right)_V$$ 3

The first partial derivative on the right of the equality is given by Eq. 7.6.16. The second partial derivative in Eq. 3 can be inverted to find a more familiar form (see Problem 14 and Problem 15 Eqs. 2-4):

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} \quad \text{or inverting:} \quad \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_v} \qquad\qquad 4$$

Substituting α/κ_T and Eq. 4 into Eq. 3 gives the final result:

$$\left(\frac{\partial P}{\partial S}\right)_V = \frac{\alpha\,T}{\kappa_T\,C_v} \qquad\qquad 5$$

This partial derivative is important because it is the result of the Maxwell relationship based on the internal energy, Eq. 16.4.8. The Maxwell relationship and Eq. 5 allow the derivative involving the entropy to be expressed entirely in terms of a heat capacity, α, and κ_T.

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.

Answer: The plan is to note that partial derivatives involving entropy can often be simplified using a Maxwell relationship.

The Maxwell relation based on the internal energy, Eq. 16.4.8, relates the required partial derivative to a derivative with respect to the entropy:

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

Using Eqs. 1-5 in the last problem gives the required partial derivative as:

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

(b). For an ideal gas, $P = nRT/V$ giving $(\partial P/\partial T)_V = nR/V$:

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

Separating variables gives:

$$C_v \frac{dT}{T} = -nR\frac{dV}{V} \quad \text{and integrating:} \quad C_v \int_{T_1}^{T_2} \frac{dT}{T} = -nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_v \ln\frac{T_2}{T_1} = -nR\ln\frac{V_2}{V_1} \qquad\qquad (9.8.12°)$$

Eq. 9.8.12° was originally derived using explicit consideration of the heat and work transfers. The derivation in this problem more clearly shows the relationship of the overall changes to the

constancy of the entropy for the process. Since entropy is a state function, the overall process can be broken into the sum of a constant volume process and a constant temperature process, with the same initial and final conditions. The first term in Eq. 9.8.12° is the change in entropy for a constant volume process and the second term is the negative of the change in entropy for an isothermal process in an ideal gas. The two changes are equal in magnitude and opposite in sign so that the overall change in entropy is zero.

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.

Answer: The plan is to note that partial derivatives involving entropy can often be simplified using a Maxwell relationship.
   The Maxwell relation based on the enthalpy, Eq. 16.4.9, relates the required partial derivative to a derivative with respect to the entropy:

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

Using Problem 20, Eqs. 1-5, gives the required partial derivative as:

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

(b). For an ideal gas, $V = nRT/P$ giving $(\partial V/\partial T)_P = nR/P$:

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{nR}{P}\right)\left(\frac{T}{C_P}\right)$$

Separating variables gives:

$$C_P \frac{dT}{T} = nR \frac{dP}{P} \qquad \text{and integrating:} \qquad C_P \int_{T_1}^{T_2} \frac{dT}{T} = nR \int_{P_1}^{P_2} \frac{dP}{P}$$

$$C_P \ln \frac{T_2}{T_1} = nR \ln \frac{P_2}{P_1} \qquad\qquad\qquad (9.8.18°)$$

Eq. 9.8.18° was originally derived using the change in enthalpy for the process. The derivation in this problem more clearly shows the relationship of the overall changes to the constancy of the entropy for the process. Since entropy is a state function, the overall process can be broken into the sum of a constant pressure process and a constant temperature process, with the same initial and final conditions. The first term in Eq. 9.8.18° is the change in entropy for a constant pressure process and the second term is the negative of the change in entropy for an isothermal process in

an ideal gas. The two changes are equal in magnitude and opposite in sign so that the overall change in entropy is zero.

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:[2]

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

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

Answer: The plan is to note that partial derivatives involving entropy can often be simplified using a Maxwell relationship.
(a). The Maxwell relation based on the enthalpy, Eq. 16.4.9, relates the required partial derivative to a derivative with respect to the entropy:

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

Using Problem 20, Eqs. 1-6, gives the required partial derivative as:

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

(b). The heat capacity is usually expressed as a molar value; the molar volume of benzene is:

$$V_o = 1 \text{ mol}(78.11 \text{ g mol}^{-1})(1 \text{ m}^3/1\times10^6 \text{ cm}^3)/0.8765 \text{ g cm}^{-3} = 8.912\times10^{-5} \text{ m}^3$$

Substituting the required values and solving for C_p gives:

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{0.0484 \text{ K}}{2.02\times10^5 \text{Pa}} = \frac{TV\alpha}{C_p} = \frac{298.15 \text{ K}(8.912\times10^{-5} \text{ m}^3)(1.24\times10^{-3} \text{ K}^{-1})}{C_p}$$
$$C_p = 137.5 \text{ J K}^{-1} \text{ mol}^{-1}$$

This expression shows the importance of the Maxwell relationships in their ability to uncover relationships among important system properties. This relationship is also important in modeling the mechanism of impulse welding techniques. In impulse welding, two dissimilar metals are accelerated towards each other by an explosion, an intense magnetic field pulse, or a laser pulse. The impact creates a large pressure, up to 1×10^9 Pa, that plastically deforms and heats the materials. For example, explosion welding is necessary to fabricate components of high field magnet dewars for NMR.

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

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

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

Answer: (a). The plan is to integrate Eq. 7.6.9 for small changes in pressure (see Problem 7.11) and then use the volume as a function of pressure in $\Delta G = \int V \, dP$ (see Problem 1, above, in comparision).
   Reviewing Problem 7.11, integrating $dV = -V \kappa_T \, dP$ from V_o, P_o to V, P gives:

$$\int_{V_o}^{V} dV = - \int_{P_o}^{P} V \kappa_T \, dP$$

For small changes in pressure, we can approximate the volume in the integrand as $V \approx V_o$:

$$V - V_o = - \int_{P_o}^{P} V_o \kappa_T \, dP = - V_o \kappa_T (P - P_o) \qquad \text{and} \qquad V = V_o - V_o \kappa_T (P - P_o)$$

Using this last expression for the volume as a function of pressure in $\Delta G = \int V \, dP$ gives:

$$\Delta G = \int_{P_o}^{P} [V_o - V_o \kappa_T (P - P_o)] \, dP = \int_{P_o}^{P} V_o \, dP - \int_{P_o}^{P} V_o \kappa_T (P - P_o) \, dP$$

$$= V_o (P - P_o) - \tfrac{1}{2} V_o \kappa_T (P - P_o)^2 \big|_{P_o}^{P}$$

$$= V_o (P - P_o) - \tfrac{1}{2} V_o \kappa_T (P - P_o)^2 - \tfrac{1}{2} V_o \kappa_T (P_o - P_o)^2$$

$$= V_o (P - P_o) - \tfrac{1}{2} V_o \kappa_T (P - P_o)^2$$

(b). The second term in the last expressions is a correction term for the approximate formula that was derived in Problem 1. Using Table 7.6.1, $\kappa_T = 4.53 \times 10^{-5}$ bar^{-1} = 4.53×10^{-10} Pa^{-1} for water:

$$\Delta G = 0.07021 \ \text{m}^3 \ (-1.00 \times 10^5 \ \text{Pa}) - \tfrac{1}{2}(0.07021 \ \text{m}^3)(4.53 \times 10^{-10} \ \text{Pa}^{-1})(-1.00 \times 10^5 \ \text{Pa})^2$$
$$= -7021. \ \text{J} - 0.32 \ \text{J} = -7.02 \ \text{kJ}$$

The correction is negligible for small changes in pressure, but important for work under extreme conditions in geochemistry and chemical engineering.

26. (a). Calculate the change in internal energy for one mole of liquid water for an isothermal decrease in volume from 1.0000 L to 0.9900 L at 298.2 K and an initial pressure of 1.00 bar. Assume that α and κ_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.

Answer: The plan is to follow Example 16.5.1, but using the thermodynamic equation of state for the change in internal energy with respect to volume, Eq. 16.5.8:

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

Substituting for P and integrating Eq 16.5.8 gives:

$$\Delta U = -\int_{V_o}^{V} P\,dV + \int_{V_o}^{V} T\frac{\alpha}{\kappa_T}dV = -\int_{V_o}^{V} P_o\,dV + \int_{V_o}^{V} \frac{1}{V_o\,\kappa_T}(V - V_o)\,dV + \int_{V_o}^{V} T\frac{\alpha}{\kappa_T}dV$$

Given that α and κ_T are assumed constant over this volume range, for an isothermal process:

$$\Delta U = -P_o\,\Delta V + \frac{1}{2\,V_o\,\kappa_T}(V - V_o)^2 + T\frac{\alpha}{\kappa_T}\Delta V$$

The pure molar volume for water at 25°C is (1.00 mol)(18.02 g mol^{-1})/0.99705 g mL^{-1} = 18.07 mL = 18.07x10^{-6} m^3. From Table 7.6.1 and using 1 bar = 1x10^5 Pa, α = 2.57x10^{-4} K^{-1}, κ_T = 4.53x10^{-5} bar^{-1} = 4.53x10^{-10} Pa^{-1}, ΔV = (1.0000 – 0.9900 L) = -0.0100 L = -1.00x10^{-5} m^3, giving:

$$\Delta U = -1.00\text{x}10^5\text{ Pa}(-1.00\text{x}10^5\text{ m}^3) + \frac{1}{2(1.00\text{x}10^{-3}\text{ m}^3)(4.53\text{x}10^{-10}\text{ Pa}^{-1})}(-1.00\text{x}10^{-5}\text{ m}^3)^2 +$$

$$298.2\text{ K}\frac{2.57\text{x}10^{-4}\text{ K}^{-1}}{4.53\text{x}10^{-10}\text{ Pa}^{-1}}(-1.0\text{x}10^{-5}\text{ m}^3)$$

$$\Delta U = 1.00\text{ J} + 110.4\text{ J} - 1691\text{ J} = -1.58\text{x}10^3\text{ J} = -1.58\text{ kJ}$$

The first two terms are the PV work for the compression, which increases the internal energy. The third term is the change in internal energy caused by the change in entropy with respect to volume. As the volume decreases the entropy decreases, especially with respect to the intermolecular forces, which correspondingly decreases the internal energy by TdS.

(b). The final pressure is:

$$P = P_o - \frac{1}{V_o\,\kappa_T}(V - V_o) = 1.00\text{x}10^{-5}\text{ Pa} - \frac{1}{1.00\text{x}10^{-3}\text{ m}^3(4.53\text{x}10^{-10}\text{ Pa}^{-1})}(-1.00\text{x}10^5\text{ m}^3)$$

$$P = 2.2175\text{x}10^7\text{ Pa} = 222.\text{ bar}$$

The compression requires a large increase in pressure, comparable to the increase in pressure generated while ice skating.

<u>27</u>. Calculate the change in Gibbs energy of a liquid substance with isothermal compressibility κ_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 κ_T is constant.

Answer: The plan is to note that since the natural variables for G are P and T, the "misplaced" variable is V as the independent variable in the denominator.
  Reference to Figure 9.7.1 suggests using the chain rule:

$$\left(\frac{\partial G}{\partial V}\right)_T = \left(\frac{\partial G}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$$

The partial $(\partial G/\partial P)_T$ is the thermodynamic force, $(\partial G/\partial P)_T = V$. From the definition of the isothermal compressibility, Eq. 7.6.9:

$$\kappa_T = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T \qquad \text{or inverting:} \qquad \left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{1}{-V\kappa_T}\right)$$

Substituting this last result and the thermodynamic force gives:

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

This expression is listed in the table Figure 16.4.1. Integration for constant κ_T gives:
$\Delta G = - (1/\kappa_T)\,\Delta V$.

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

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

Answer: The plan is to follow Eqs. 16.3.9-16.3.10, but for constant volume processes.
  Consider A/T as the product $(A)(1/T)$ and use the product rule:

$$\left(\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right)_V = A\left(\frac{\partial\left(\frac{1}{T}\right)}{\partial T}\right)_V + \frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_V = -\frac{A}{T^2} + \frac{1}{T}\left(\frac{\partial A}{\partial T}\right)_V$$

Using Eq. 16.3.7 for the thermodynamic force, $(\partial A/\partial T)_V = - S$, gives:

$$= -\frac{A}{T^2} - \frac{S}{T}$$

Then taking T^2 as the common denominator gives:

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

The definition of the Helmholtz energy is $A \equiv U - TS$. Rearrangement of the definition gives $A + TS = U$, which upon substitution simplifies to:

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

29. Rewrite Figure 9.7.1 for the partial derivatives:

$$\left(\frac{\partial \mathbf{G}}{\partial T}\right)_V \qquad \left(\frac{\partial \mathbf{T}}{\partial G}\right)_P \qquad \left(\frac{\partial \mathbf{G}}{\partial V}\right)_T \qquad \left(\frac{\partial \mathbf{G}}{\partial T}\right)_V \qquad \left(\frac{\partial \mathbf{P}}{\partial T}\right)_{\mathbf{G}}$$

Answer: The plan is to rewrite Figure 9.7.1 using the same five partial derivative conversion techniques, α, κ_T, and the thermodynamic forces, Eqs. 16.3.7 and 16.3.8:

$$\left(\frac{\partial A}{\partial T}\right)_V = -S \qquad \left(\frac{\partial G}{\partial P}\right)_T = V \quad \text{and} \quad \left(\frac{\partial G}{\partial T}\right)_P = -S$$

The conversion for $(\partial G/\partial V)_T$ is given in Problem 24. The partial derivative conversions are shown below:

$$\left(\frac{\partial \mathbf{G}}{\partial T}\right)_V = \left(\frac{\partial A}{\partial T}\right)_V + \left(\frac{\partial P}{\partial T}\right)_V V = -S + V\alpha/\kappa_T \qquad \left(\frac{\partial \mathbf{T}}{\partial G}\right)_P = \frac{1}{\left(\frac{\partial G}{\partial T}\right)_P} = -\frac{1}{S}$$

$$G \equiv A + PV$$

definition
misplaced numerator

invert
misplaced numerator

$$\left(\frac{\partial \mathbf{G}}{\partial T}\right)_V \qquad \left(\frac{\partial \mathbf{T}}{\partial G}\right)_P$$

$$\left(\frac{\partial \mathbf{G}}{\partial V}\right)_T \qquad \left(\frac{\partial \mathbf{G}}{\partial T}\right)_V \qquad \left(\frac{\partial \mathbf{P}}{\partial T}\right)_{\mathbf{G}}$$

misplaced denominator
chain rule

misplaced constant variable
total differential, dG

misplaced constant variable
total differential, dG = 0

$$\left(\frac{\partial G}{\partial V}\right)_T = \left(\frac{\partial G}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$$

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

$$= -\frac{1}{\kappa_T}$$

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

$$\left(\frac{\partial G}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P + \left(\frac{\partial G}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

$$= -S + V\alpha/\kappa_T$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP = 0$$

$$\left(\frac{\partial G}{\partial T}\right)_P + \left(\frac{\partial G}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{\mathbf{G}} = 0$$

$$\left(\frac{\partial P}{\partial T}\right)_{\mathbf{G}} = \frac{-\left(\frac{\partial G}{\partial T}\right)_P}{\left(\frac{\partial G}{\partial P}\right)_T} = \frac{S}{V}$$
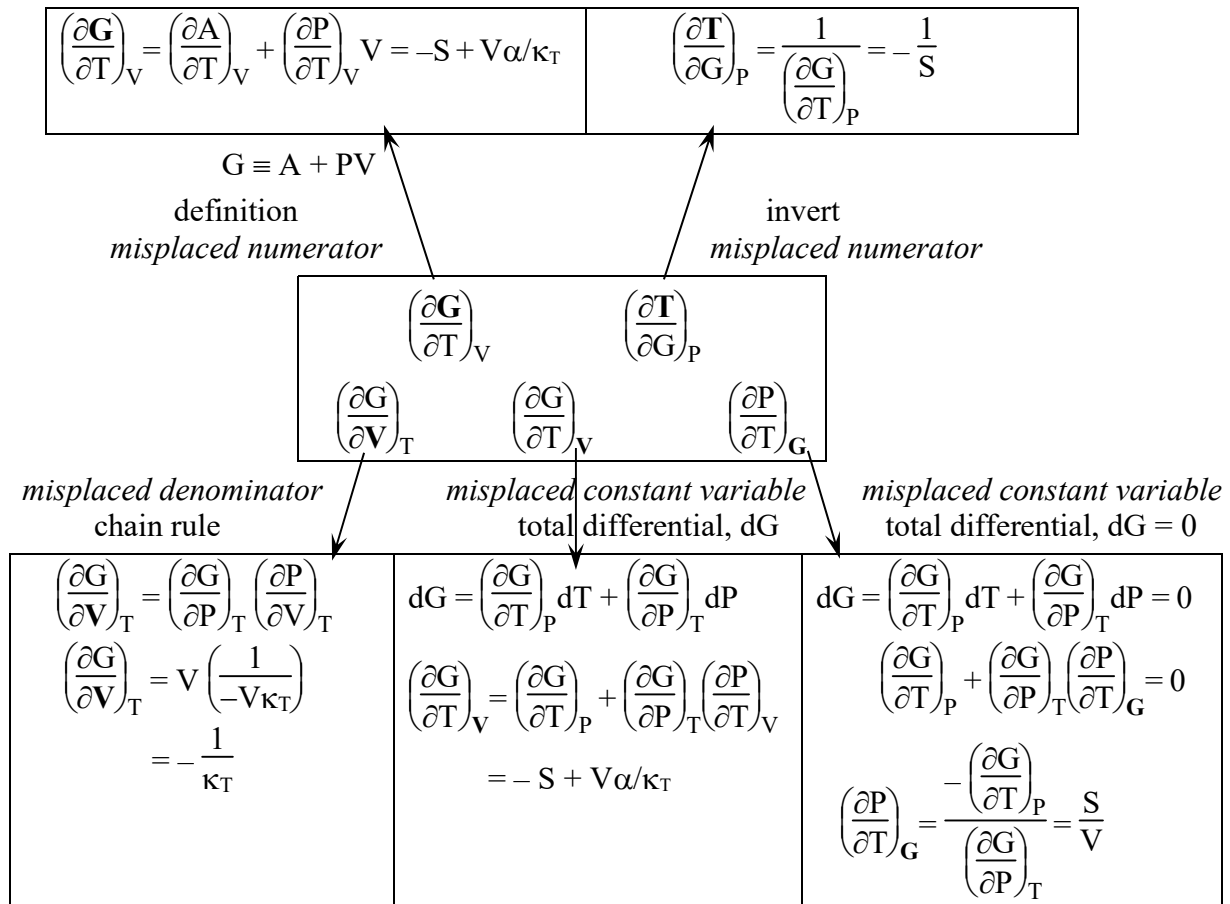
Figure P29.1: Partial Derivative Conversion. Partial derivative manipulations to convert unknown partial derivatives to those involving C_v, C_p, α, and κ_T.

The last example, using the Euler chain relationship, is used with equilibrium phase transitions of pure substances. For a phase transition at equilibrium, $\Delta_{tr}G = 0$ and then the change in pressure

necessary for the system to remain at equilibrium for a change in temperature is given using *General Pattern* ℘ **8**:

$$\left(\frac{\partial P}{\partial T}\right)_G = \frac{\Delta_{tr}S}{\Delta_{tr}V} \qquad (17.1.7)$$

where $\Delta_{tr}S$ is the entropy change for the phase transition and $\Delta_{tr}V$ is the change in molar volume. This last result gives Eq. 17.1.7, which is one form of the famous Clapeyron equation.

<u>30</u>. 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 ΔU for an isothermal expansion from V_1 to V_2.

Answer: The plan is to integrate the thermodynamic equation of state, Eq. 16.5.5:

$$\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V \qquad 1$$

The Van der Waals equation of state, Eq. 7.5.1, rearranges to give:

$$P = \frac{nRT}{(V-nb)} - a\frac{n^2}{V^2} \qquad 2$$

The mechanical derivative is:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{(V-nb)} \qquad 3$$

Using this partial derivative and the Van der Waals equation, Eq. 2, to substitute for P into the thermodynamic equation of state, Eq. 3, gives:

$$\left(\frac{\partial U}{\partial V}\right)_T = -\frac{nRT}{(V-nb)} + \frac{an^2}{V^2} + T\frac{nR}{(V-nb)} = \frac{an^2}{V^2} \qquad 4$$

We can now separate variables and integrate:

$$dU = \frac{an^2}{V^2}\,dV \qquad \text{giving:} \qquad \int_{U_1}^{U_2} dU = \int_{V_1}^{V_2}\frac{an^2}{V^2}\,dV \qquad 5$$

Using $\int \frac{1}{x^2}\,dx = -\frac{1}{x}$ gives:

$$\Delta U = -a\,n^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \qquad 6$$

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

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

$k=$"stretchiness"
x= extension

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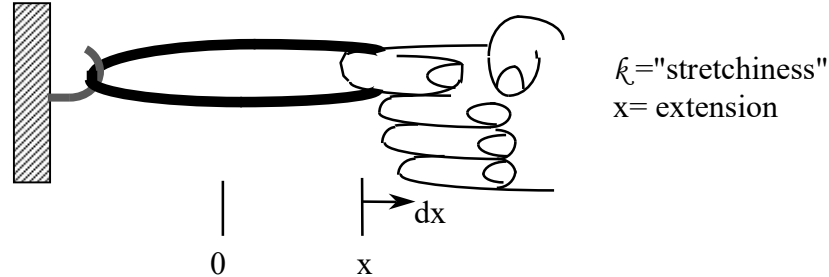
(a). Under what conditions is ΔG be a good spontaneity criterion (i.e. when what is held constant)? (b). For an initial state with a stretched rubber band, $x > 0$, find the direction for spontaneous change, either $dx > 0$ or $dx < 0$, at constant temperature and pressure. (c). Define a new state function: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

Answer: (a). ΔG is a good spontaneity criterion at constant T and P. Setting T and P as constant gives $dG = -F\,dx$, which focuses attention on the work of extension.
(b). For a spontaneous process at constant T and P, $dG = -F\,dx < 0$. Substituting in the force, $F = -kx$, gives:

$$dG = kx\,dx < 0$$

For an initial stretched state with $x > 0$, then $dx < 0$ to make dG negative overall. With $dx < 0$ the rubber band relaxes toward $x = 0$, the equilibrium position, as expected.
 (c). This definition is a Legendre transformation. Taking the total differential using the product rule gives:

$$dR = dG + F\,dx + x\,dF$$

Substituting in for dG gives:

$$dR = -S\,dT + V\,dP - F\,dx + F\,dx + x\,dF$$

Canceling terms gives:

$$dR = -S\,dT + V\,dP + x\,dF$$

The independent variables are T, P, and F. This function would be useful for systems that have extension work with a constant force and then some other form of work, in addition. The additional work might be chemical work, for example in a muscle.

<u>32</u>. 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 <u>any</u> process in an ideal gas. (At first it doesn't look like $dU = TdS - PdV$ will give just $dU = C_v\,dT$, does it?)

Answer: Substituting for dS into the combined First and Second Laws gives:

$$dU = TdS - PdV = T\left(\frac{C_v}{T}\,dT + \frac{nR}{V}\,dV\right) - PdV$$

$$dU = C_v\,dT + \frac{nRT}{V}\,dV - PdV$$

However, for an ideal gas $P = nRT/V$ and the last two terms cancel:

$$dU = C_v\,dT + \frac{nRT}{V}\,dV - \frac{nRT}{V}\,dV = C_v\,dT$$

The only restriction we have placed on this equation is that the system is an ideal gas.

<u>33</u>. 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:

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

Answer: The plan is to relate dG and dH using the definition of the Gibbs energy, $G \equiv H - TS$. In other words, treat the G in the numerator as "misplaced."

   No generality will be lost if we consider only a single component, but the notation will be simplified. Substituting the definition of the Gibbs energy gives:

$$\left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial H}{\partial n}\right)_{T,P} - T\left(\frac{\partial S}{\partial n}\right)_{T,P} \qquad\qquad 1$$

Considering $(\partial H/\partial n)_{T,P}$, the natural variables for H are S and P, not the given independent variables T and P. We can treat the constant T as the "misplaced" variable. Consulting Figure 9.7.2, we need to work through the total differential of the enthalpy expressed as a function of independent variables, S, P, and n:

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,n}dS + \left(\frac{\partial H}{\partial P}\right)_{T,n}dP + \left(\frac{\partial H}{\partial n}\right)_{S,P}dn \qquad\qquad 2$$

Dividing by dn at constant T and P gives the desired enthalpy derivative. With $dP = 0$ and using the fact that $(\partial H/\partial S)_{P,n}$ is a thermodynamic force, $(\partial H/\partial S)_{P,n} = T$:

$$\left(\frac{\partial H}{\partial n}\right)_{T,P} = \left(\frac{\partial H}{\partial S}\right)_{P,n}\left(\frac{\partial S}{\partial n}\right)_{T,P} + \left(\frac{\partial H}{\partial n}\right)_{S,P} = T\left(\frac{\partial S}{\partial n}\right)_{T,P} + \left(\frac{\partial H}{\partial n}\right)_{S,P} \qquad\qquad 3$$

Substitution of Eq. 3 into Eq. 1 gives the desired result after cancellation:

$$\left(\frac{\partial G}{\partial n}\right)_{T,P} = T\left(\frac{\partial S}{\partial n}\right)_{T,P} + \left(\frac{\partial H}{\partial n}\right)_{S,P} - T\left(\frac{\partial S}{\partial n}\right)_{T,P} = \left(\frac{\partial H}{\partial n}\right)_{S,P} \qquad 4$$

The other equalities of the chemical potentials, in terms of the corresponding natural variables in Eqs. 16.6.14, can be proved in an analogous fashion.

<u>34</u>. 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.

Answer: Using Eqs. 18.2.9° and 18.2.10°:

$$\Delta_{mix}S = - n_{tot}R \sum_{i=1}^{n_s} y_i \ln y_i = - 1.00 \text{ mol}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})[0.80 \ln 0.80 + 0.20 \ln 0.20]$$
$$= 4.16 \text{ J K}^{-1}$$

$$\Delta_{mix}G = - T \Delta_{mix}S = - 298.15 \text{ K}(4.16 \text{ J K}^{-1})(1 \text{ kJ}/1000 \text{ J}) = -1.24 \text{ kJ mol}^{-1}$$

<u>35</u>. 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.

Answer: For one total mole of air as a feed gas for a fossil fuel based power plant or automobile, assuming complete conversion of the O_2 to CO_2 gives a final exhaust gas that is 20.9 mol% CO_2 and 79.1 mol% N_2. The negative of the Gibbs energy of mixing is the minimum work necessary to separate the CO_2 from the N_2:

$$\Delta_{mix}G = n_{tot}RT \sum_{i=1}^{n_s} y_i \ln y_i$$
$$= 1.00 \text{ mol}(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K})[0.209 \ln 0.209 + 0.791 \ln 0.791]$$
$$= -1.27_1 \text{ kJ}$$

Per mole of CO_2 produced: $\Delta_{mix}G_m(CO_2) = -1.27_1$ kJ/0.209 mol = -6.08 kJ mol^{-1} of CO_2.

The energy required to separate the CO_2 and N_2 is then +6.08 kJ mol^{-1}. The separation is likely to be facilitated using a ceramic membrane based on a zeolite-type molecular sieve material. The Gibbs energy of combustion of carbon graphite, by comparison, yields:

$$C(graph) + O_2 \text{ (g, 1 bar)} \rightarrow CO_2 \text{ (g, 1 bar)} \qquad \Delta_f G_{298 K}^{\circ} = -394.36 \text{ kJ mol}^{-1}$$

The Gibbs energy of combustion of graphite is equivalent to the Gibbs energy of formation of CO_2. The separation requires at least 1.5% of the energy produced by the combustion. The energy lost in separating CO_2 from the exhaust stream is minimal under ideal conditions. However, the CO_2 produced is at low pressure, 1 bar, and must be liquefied or otherwise compacted for disposal.

<u>36</u>. 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 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 CO_2 at 150 bar and 304.14 K, and compare to the result using Figure 16.7.1 (see Example 16.7.1).

Answer: The plan is to use Eq. 16.7.9 with the given Virial polynomial expansion for the compressibility factor.
   Substituting the Virial expansion through the second Virial coefficient into Eq. 16.7.9 gives the integral as:

$$\ln f/_P = \int_0^P \frac{(z-1)}{P} dP = \int_0^P \frac{B(T)}{RT} dP = \frac{B(T)}{RT} P$$

With $f = \gamma P$, then $f/_P = \gamma$. For the given conditions:

$$\ln \gamma = \frac{-0.114 \text{ L mol}^{-1}}{0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1} \, 304.14 \text{ K}} \, 150 \text{ bar} = -0.6762$$
$$\gamma = 0.509$$

The reduced temperature is $T_R = T/T_c = 1$ and the reduced pressure is $P_R = P/P_c$. The critical pressure for CO_2 is 73.843 bar, giving $P_R = 150 \text{ bar}/73.843 \text{ bar} = 2.03$. Reading the fugacity coefficient from Figure 16.7.1 gives $\gamma \cong 0.43$. Our result of $\gamma = 0.509$ is sufficiently close given that only the second Virial coefficient term was retained in this approximation. Notice when only the second Virial coefficient term is retained that $\ln \gamma = z - 1$.

<u>37</u>. A brief outline of carbon sequestration is given in Problem 32. One proposal for carbon sequestration is to pump liquid or super critical CO_2 deep underground into abandoned oil wells that are sealed by salt domes. CO_2 may be liquefied at temperatures less than the critical temperature and pressures greater than the critical pressure. For 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 CO_2. At equilibrium, the chemical potential of the liquid is equal to the chemical potential of the vapor, $\mu_{CO_2}^*(l) = \mu_{CO_2}(g)$. Find the chemical potential for 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.

Answer: Reading the fugacity coefficient from Figure 16.7.1 gives $\gamma \cong 0.666$ for $T_R = 1.00$ and $P_R = 1.00$. Using Eq. 16.7.1 the chemical potential is given by:

for real CO_2:

$$\mu_A = \mu_A^\circ(g) + RT \ln f/p^\circ = \mu_A^\circ(g) + RT \ln \gamma P/p^\circ$$
$$= \mu_A^\circ(g) + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(304.14 \text{ K})(1 \text{ kJ}/1000 \text{ J}) \ln[0.666(73.843 \text{ bar})/1 \text{ bar}]$$
$$= \mu_A^\circ(g) + 9.85 \text{ kJ mol}^{-1} \hspace{4cm} \text{(real)}$$

for ideal CO_2:

$$\mu_A = \mu_A^\circ(g) + RT \ln P/p^\circ = \mu_A^\circ(g) + 10.88 \text{ kJ mol}^{-1} \hspace{2cm} \text{(ideal)}$$

Attractive intermolecular forces decrease the chemical potential of the real vapor and liquid as compared to the ideal vapor. Notice that in this problem we have not calculated the PV work necessary to condense CO_2. However, we can use the fugacity coefficient as a general indication of the importance of intermolecular forces.

<u>38</u>. 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:

$$CaCO_3 \text{ (s)} \rightarrow CaO \text{ (s)} + CO_2 \text{ (g, P = 50.0 bar)}$$
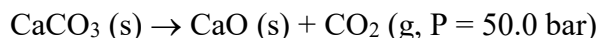
Approximate the fugacity coefficient using:

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

where B(T) is the second Virial coefficient at the given temperature (see Problem 36 for the justification). For 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).

Answer: Under standard state conditions:

	$CaCO_3$ (s)	$\rightarrow$	CaO (s)	+	CO_2 (g, $P^\circ = 1$ bar)
$\Delta_f G^\circ$	-1128.8		-604.03		-394.36 kJ mol^{-1}
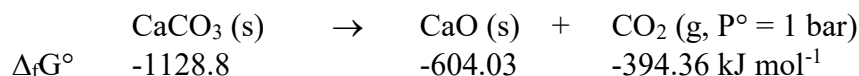
$$\Delta_r G^\circ = \sum_{i=1}^{n_s} \nu_i \Delta_f G^\circ = [\Sigma \text{products}] - [\Sigma \text{reactants}]$$
$$= [(-394.36) + (-604.03)] - [-1128.8] \text{ kJ mol}^{-1} = 130.41 \text{ kJ mol}^{-1}$$

The Gibbs energy of each <u>gaseous</u> reactant and product is then adjusted for the new pressure:

$$\Delta_r G = \Delta_r G^\circ + \sum \nu_i RT \ln f_i/p^\circ \hspace{3cm} (\nu_i \text{ for gases only})$$

The ν_i are the stoichiometric coefficients for each gaseous reactant and product, with ν_i negative for reactants. (See Chapter 20 for more information on non-standard state reaction Gibbs energies). For this reaction $\nu_{CO_2} = 1$ is the only gas:

$$\Delta_r G = \Delta_r G^\circ + RT \ln f/p^\circ$$

For the given conditions:

$$\ln \gamma = \frac{-0.125 \text{ L mol}^{-1}}{0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1} \ 298.15 \text{ K}} \ 50 \text{ bar} = -0.2521$$

$$\gamma = 0.777$$

$$\Delta_r G = \Delta_r G^\circ + RT \ln (0.777)(50.0 \text{ bar})/1 \text{ bar}$$
$$= 130.41 \text{ kJ mol}^{-1} + 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}(1 \text{ kJ}/1000 \text{ J})(298.15 \text{ K}) \ln 38.8_6$$
$$= 130.41 \text{ kJ mol}^{-1} + 9.07 \text{ kJ mol}^{-1} = 139.48 \text{ kJ mol}^{-1}$$

The value assuming $\gamma = 1$ is 140.11 kJ mol^{-1}, as given in Ch. 15, Problem 17.

<u>39</u>. *(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.

Answer: The plan is to find TdS and μdn for an open system in terms of T, V, and n, and then substitute into $dU = T \ dS - P \ dV + \mu \ dn$.

Consider, first, $\mu \ dn$. The chemical potential is given in terms of the natural variables, U(S,V, n), by:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV + \left(\frac{\partial U}{\partial n}\right)_{S,V} dn \qquad\qquad 1$$

Dividing by dn at constant T and V gives the molar internal energy at constant temperature and volume:

$$\left(\frac{\partial U}{\partial n}\right)_{T,V} = \left(\frac{\partial U}{\partial S}\right)_{V,n} \left(\frac{\partial S}{\partial n}\right)_{T,V} + \left(\frac{\partial U}{\partial n}\right)_{S,V} \qquad\qquad 2$$

The internal energy derivative with respect to entropy is the thermodynamic force, $(\partial U/\partial S)_{V,n} = T$. The last term, $(\partial U/\partial n)_{S,V}$, is the chemical potential, μ. Solving for the chemical potential gives:

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{T,V} - T\left(\frac{\partial S}{\partial n}\right)_{T,V} \qquad\qquad 3$$

We next need to find TdS, starting from the total differential of S in terms of T, V, and n:

$$dS = \left(\frac{\partial S}{\partial T}\right)_{V,n} dT + \left(\frac{\partial S}{\partial V}\right)_{T,n} dV + \left(\frac{\partial S}{\partial n}\right)_{T,V} dn \qquad 4$$

Note that the entropy change includes terms from the temperature change, the volume change, and the change in number of moles of substance. Note that $(\partial S/\partial T)_{V,n} = C_V/T$. We can also use the Maxwell relationship, Eq. 16.4.10, $(\partial S/\partial V)_{T,n} = (\partial P/\partial T)_{V,n}$. Then, TdS is given by:

$$T\, dS = C_V\, dT + T\left(\frac{\partial P}{\partial T}\right)_{V,n} dV + T\left(\frac{\partial S}{\partial n}\right)_{T,V} dn \qquad 5$$

Substituting Eqs. 3 and 5 into $dU = T\, dS - P\, dV + \mu\, dn$ gives:

$$dU = C_V\, dT + T\left(\frac{\partial P}{\partial T}\right)_{V,n} dV + T\left(\frac{\partial S}{\partial n}\right)_{T,V} dn - P\, dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn - T\left(\frac{\partial S}{\partial n}\right)_{T,V} dn \qquad 6$$

$$dU = C_V\, dT + T\left(\frac{\partial P}{\partial T}\right)_{V,n} dV - P\, dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn \qquad 7$$

Distributing out the common factor of dV gives:

$$dU = C_V dT + \left[-P + T\left(\frac{\partial P}{\partial T}\right)_{V,n}\right] dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn \qquad 8$$

The term in brackets is the thermodynamic equation of state for the internal energy, $(\partial U/\partial V)_{T,n}$, Eq. 16.5.5:

$$dU = C_V\, dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn \qquad 9$$

This derivation shows that $dU = T\, dS - P\, dV + \mu\, dn$ and Eq. 9 are consistent and can be derived from each other. The derivation of Eqs. 4 and 5 show that both the TdS and the μ dn terms depend on the change in number of moles of the substance.

(b). At constant temperature and volume, Eq. 9 reduces to:

$$dU = \left(\frac{\partial U}{\partial n}\right)_{T,V} dn \qquad \text{(cst. T\&V)} \qquad 10$$

where the partial derivative is the well-known molar internal energy of the substance. For a chemical reaction, the molar internal energy of the products minus the reactants gives the conventional $\Delta_r U$.

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:

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

Answer: The plan is to write the total differential of S as a function of T, P, and n, and then use a Maxwell Relationship for one of the entropy derivatives.
   Starting from the total differential of the entropy in terms of T, P, and n:

$$dS = \left(\frac{\partial S}{\partial T}\right)_{P,n} dT + \left(\frac{\partial S}{\partial P}\right)_{T,n} dP + \left(\frac{\partial S}{\partial n}\right)_{T,P} dn \qquad 1$$

Note that $(\partial S/\partial T)_{P,n} = C_p/T$. We can also use the Maxwell relationship, Eq. 16.4.11, $(\partial S/\partial P)_{T,n} = -(\partial V/\partial T)_{P,n}$ and the definition of the molar entropy, $(\partial S/\partial n)_{T,P} = S_m$. Substituting these values into Eq. 1 gives TdS as:

$$T\ dS = C_p\ dT - T\left(\frac{\partial V}{\partial T}\right)_{P,n} dP + T\ S_m\ dn \qquad 2$$

which can also be expressed as:

$$T\ dS = C_p\ dT - TV\alpha\ dP + T\ S_m\ dn \qquad 3$$

Eqs. 2 and 3 show that both the TdS and μ dn terms depend on the change in number of moles of the substance.

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.

Answer: (a). Substituting Eq. 2 from the last problem into $dH = T\, dS + V\, dP + \mu\, dn$ gives:

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

Factoring out the common factor of dP gives:

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

The term in brackets is the thermodynamic equation of state for the enthalpy, $(\partial H/\partial P)_{T,n}$, Eq. 16.5.11:

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

(b). The chemical potential, based on the enthalpy is given by Eq. 16.6.14 as:

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

since the natural variables for H are S and P. The conventional molar enthalpy of a substance listed in reference tables, $(\partial H/\partial n)_{T,P}$, is at constant T and P, however. The "misplaced" variable is the constant T. To find the conventional molar enthalpy, we work from the total differential of H with respect to the natural variables:

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,n} dS + \left(\frac{\partial H}{\partial P}\right)_{S,n} dP + \left(\frac{\partial H}{\partial n}\right)_{S,P} dn$$

Dividing by dn at constant T and P gives the conventional molar enthalpy:

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

The first partial on the right of the equality is the thermodynamic force, $(\partial H/\partial S)_{P,n} = T$. The entropy derivative is the conventional molar entropy S_m. The last term is the chemical potential. Solving for the chemical potential gives:

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

This last expression can also be written as $\mu = H_m - T\, S_m$, as expected from the definition, $G \equiv H - TS$. This expression was also proved in Problem 33, Eq. 1 or Eq. 3.

(c). Combining this last expression for the chemical potential with dH from part (a) gives:

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

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

Substituting the definition of $C_p \equiv (\partial H/\partial T)_{P,n}$ back into this last expression gives:

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

This result, which was derived from $dH = T\,dS + V\,dP + \mu\,dn$, is the general total differential of the enthalpy with respect to independent variables T, P and n. This equality shows that dH derived from H(S,P,n) and H(T,P,n) are equivalent, as they must be.

(d). At constant T and P, dH reduces to:

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

where $(\partial H/\partial n)_{T,P} \equiv H_m$ is the conventional molar enthalpy of the substance as found in standard reference tables. While these results are intuitive and expected, the interpretation of the TdS term in $dH = T\,dS + V\,dP + \mu\,dn$ and the relationship to the constant temperature and pressure molar enthalpy is a common source of confusion, even for experienced physical chemists.

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