

CHM 3400 – Problem Set 2

Due date: Wednesday, January 29th.

Do all of the following problems. Show your work.

“Thermodynamics is a funny subject. The first time you go through it, you don’t understand it at all. The second time you go through it, you think you understand it, except for one or two points. The third time you go through it, you know you don’t understand it, but by that time you are so used to the subject, it doesn’t bother you anymore.”

- Arnold Sommerfeld

1) Consider a nonideal gas obeying the following equation of state (an example of a virial equation)

$$\frac{pV}{nRT} = 1 + \frac{nB}{V} + \frac{n^2C}{V^2} \quad (1.1)$$

where B and C are constants whose values only depend on temperature.

a) Find a general expression for w (work) for the isothermal reversible expansion or compression of n moles of the above substance from an initial volume V_i to a final volume V_f .

b) Using your result in part a, find the value for w when 1.000 mol of argon gas is compressed isothermally and reversibly from an initial volume $V_i = 20.00$ L to a final volume $V_f = 0.200$ L, at a temperature $T = 300.0$ K. For argon at $T = 300.0$ K, $B = -21.7$ cm³/mol and $C = 1200.$ cm⁶/mol². Give your final answer in units of J.

c) Find the value for w for the same process, but assuming that argon obeys the ideal gas law. Give your final answer in units of J.

d) Compare your answers in b and c. What is the percent difference between the result found in b and that found in c?

2) Consider the following function of two variables

$$F(x,y) = 4x^3y + 7xy^2 + 3y^2 - 6x + 2 \quad (2.1)$$

Find the following:

a) $(\partial F/\partial x)_y$

b) $(\partial F/\partial y)_x$

3) The effect of temperature on the molar volume of a liquid is often written as follows

$$V_m = V_{m,0} [1 + a (T - T_0) + b (T - T_0)^2] \quad (3.1)$$

where $V_{m,0}$ is the molar volume at a reference temperature T_0 , and a and b are constants.

a) Find an expression for α , the coefficient of thermal expansion, for a liquid whose volume is given by eq 3.1. Note that α is defined by the expression

$$\alpha = (1/V_m) (\partial V_m/\partial T)_p \quad (3.2)$$

b) For water, in the temperature range 15-35 °C, the values for the constants in eq 3.1 are $T_0 = 20.0$ °C, $a = 2.037 \times 10^{-4}$ K⁻¹, $b = 5.0 \times 10^{-6}$ K⁻², and $V_{m,0} = 18.0478$ cm³/mol. Based on this information, find the value for α (including correct units) for water at $T = 20.0$ °C and at $T = 30.0$ °C.

4) The temperature dependence of the constant pressure molar heat capacity of a pure substance ($C_{p,m}$) is often fit to the following equation (see Atkins, section 2D.3).

$$C_{p,m} = a + bT + (c/T^2) \quad (4.1)$$

where a, b, and c are constants.

a) Find the value for $C_{p,m}$ for $\text{CO}_2(\text{g})$ at $T = 300.0 \text{ K}$ and $T = 400.0 \text{ K}$. Note that for $\text{CO}_2(\text{g})$, $a = 44.22 \text{ J/mol}\cdot\text{K}$, $b = 8.79 \times 10^{-3} \text{ J/mol}\cdot\text{K}^2$, and $c = -8.62 \times 10^5 \text{ J}\cdot\text{K/mol}$.

b) Find the value for ΔH , the change in enthalpy, when 5.000 mol of $\text{CO}_2(\text{g})$ is heated from an initial temperature $T_i = 300.0 \text{ K}$ to a final temperature $T_f = 400.0 \text{ K}$ under conditions of constant pressure. Give your final answer in unit of J. (Hint – For the constant pressure heating of a pure substance $dH = n C_{p,m} dT$)

5) Using the thermochemical data given below (at $T = 25.0 \text{ }^\circ\text{C}$) find the following for the reaction



a) $\Delta H^\circ_{\text{rxn}}$ at $T = 25.0 \text{ }^\circ\text{C}$.

b) $\Delta H^\circ_{\text{rxn}}$ at $T = 100.0 \text{ }^\circ\text{C}$. To do this problem you may assume that the values for $C_{p,m}$ in the thermochemical data are constant over the range $25.0 - 100.0 \text{ }^\circ\text{C}$.

Substance	ΔH°_f (kJ/mol)	S° (J/mol·K)	ΔG°_f (kJ/mol)	$C_{p,m}$ (J/mol·K)
$\text{O}_2(\text{g})$	0.0	205.2	0.0	29.36
$\text{SnO}(\text{s})$	-285.8	56.5	-256.8	44.31
$\text{SnO}_2(\text{s})$	-580.7	52.3	-519.6	52.59

Solutions.

1) a) For mechanical (pressure-volume) work we may say

$$w = - \int_i^f p_{\text{ex}} dV$$

For a reversible process $p_{\text{ex}} = p$. For a substance whose equation of state is given by eq 1.1, since

$$\frac{pV}{nRT} = 1 + \frac{nB}{V} + \frac{n^2C}{V^2}$$

then
$$p = \frac{nRT}{V} + \frac{n^2BRT}{V^2} + \frac{n^3CRT}{V^3}$$

and so

$$w = - \int_i^f p dV = - \int_i^f \left(\frac{nRT}{V} + \frac{n^2BRT}{V^2} + \frac{n^3CRT}{V^3} \right) dV$$

Since n and T are constants, we can take a common factor of nRT outside the integral, to get

$$w = - (nRT) \int_i^f \left(\frac{1}{V} + \frac{nB}{V^2} + \frac{n^2C}{V^3} \right) dV$$

If we do the indicated integral, and evaluate the integral at the limits of integration, we get

$$w = - nRT \left\{ \ln(V_f/V_i) - nB \left[(1/V_f) - (1/V_i) \right] - (1/2) n^2C \left[(1/V_f^2) - (1/V_i^2) \right] \right\}$$

our general expression for work when a substance whose equation of state is given by eq 1.1 is isothermally and reversibly expanded or compressed.

b) Using the result from part a we can calculate the value for w for the indicated process

$$\begin{aligned} w = & - (1.000 \text{ mol}) (8.3145 \text{ J/mol}\cdot\text{K}) (300.0 \text{ K}) \left\{ \ln(0.200/20.00) \right. \\ & - (1.000 \text{ mol}) (- 0.0217 \text{ L/mol}) \left[(1/0.200 \text{ L}) - (1/20.00 \text{ L}) \right] \\ & \left. - (1/2) (1.000 \text{ mol})^2 (0.0012 \text{ L}^2/\text{mol}^2) \left[(1/0.200 \text{ L})^2 - (1/20.00 \text{ L})^2 \right] \right\} \end{aligned}$$

Note that we have converted the volume unit in the constants B and C from cm^3 to L using the relationship $1000 \text{ cm}^3 = 1 \text{ L}$.

So
$$w = - (2494.4 \text{ J}) \left\{ - 4.6052 + 0.1074 - 0.0150 \right\} = + 11257. \text{ J}$$

c) If the gas obeys the ideal gas law, then

$$w = - \int_i^f p_{\text{ex}} dV$$
 Since the process is reversible and the gas is ideal, $p_{\text{ex}} = p = nRT/V$, and so

$$\begin{aligned} w = & - \int_i^f p dV = - \int_i^f (nRT/V) dV = - nRT \ln(V_f/V_i) \\ & = - (1.000 \text{ mol}) (8.3145 \text{ J/mol}\cdot\text{K}) (300.0 \text{ K}) \ln(0.200/20.00) \\ & = + 11487. \text{ J} \end{aligned}$$

d) The ideal gas result is about 2 % larger than the result obtained using eq 1.1 For this particular gas and process the results are not much different.

- 2) a) $\partial/\partial x)_y [4x^3y + 7xy^2 + 3y^2 - 6x + 2] = 12x^2y + 7y^2 - 6$
 b) $\partial/\partial y)_x [4x^3y + 7xy^2 + 3y^2 - 6x + 2] = 4x^3 + 14xy + 6y$
- 3) a) By definition, $\alpha = (1/V_m) (\partial V_m/\partial T)_p$. So we need to find the indicated partial derivative
 $\partial/\partial T)_{V_m} \{ V_{m,0} [1 + a (T - T_0) + b (T - T_0)^2] \} V_{m,0} [a + 2b (T - T_0)]$

If we substitute this result into the definition of α , we get

$$\alpha = \frac{V_{m,0} [a + 2b (T - T_0)]}{V_{m,0} [1 + a (T - T_0) + b (T - T_0)^2]} = \frac{[a + 2b (T - T_0)]}{[1 + a (T - T_0) + b (T - T_0)^2]}$$

b) For water at $T = 20.0 \text{ }^\circ\text{C}$ (and recalling that $T_0 = 20.0 \text{ }^\circ\text{C}$)

$$\alpha = a = 2.037 \times 10^{-4} \text{ K}^{-1}$$

For water at $T = 30.0 \text{ }^\circ\text{C}$ (and noting that $T - T_0 = 30.0 \text{ }^\circ\text{C} - 20.0 \text{ }^\circ\text{C} = 10.0 \text{ }^\circ\text{C} = 10.0 \text{ K}$)

$$\alpha = \frac{[(2.037 \times 10^{-4} \text{ K}^{-1}) + 2 (5.0 \times 10^{-6} \text{ K}^{-2})(10.0 \text{ K})]}{[1 + (2.037 \times 10^{-4} \text{ K}^{-1})(10.0 \text{ K}) + (5.0 \times 10^{-6} \text{ K}^{-2})(10.0 \text{ K})^2]} = \frac{3.037 \times 10^{-4} \text{ K}^{-1}}{1.00254} = 3.029 \times 10^{-4} \text{ K}^{-1}$$

Why is the expansion of water when heated important? Well...according to the most recent IPCC report on climate change, about half of the expected rise in sea level that is predicted during the next 80 years is due to the expansion of the water currently in the ocean due to its slow increase in temperature.

4) a) We may find the values for $C_{p,m}$ by substituting into eq 4.1

$$\text{At } T = 300.0 \text{ K} \quad C_{p,m} = (44.22 \text{ J/mol}\cdot\text{K}) + (8.79 \times 10^{-3} \text{ J/mol}\cdot\text{K}^2)(300.0 \text{ K}) + (-8.62 \times 10^5 \text{ J}\cdot\text{K/mol})/(300.0 \text{ K})^2 \\ = (44.22 + 2.637 - 9.578) \text{ J/mol}\cdot\text{K} = 37.28 \text{ J/mol}\cdot\text{K}$$

$$\text{At } T = 400.0 \text{ K} \quad C_{p,m} = (44.22 \text{ J/mol}\cdot\text{K}) + (8.79 \times 10^{-3} \text{ J/mol}\cdot\text{K}^2)(400.0 \text{ K}) + (-8.62 \times 10^5 \text{ J}\cdot\text{K/mol})/(400.0 \text{ K})^2 \\ = (44.22 + 3.516 - 5.388) \text{ J/mol}\cdot\text{K} = 42.35 \text{ J/mol}\cdot\text{K}$$

Note the constant pressure molar heat capacity increases by about 14 % in going from 300.0 K to 400.0 K, a small but not insignificant change.

b) The process is carried out under conditions of constant pressure, and so

$$\Delta H = \int_{T_i}^{T_f} n C_{p,m} dT = n \int_{T_i}^{T_f} C_{p,m} dT = n \int_{T_i}^{T_f} [a + bT + c/T^2] dT \\ = n \{ a (T_f - T_i) + (b/2) (T_f^2 - T_i^2) - C [(1/T_f) - (1/T_i)] \}$$

$$\text{So } \Delta H = (5.000 \text{ mol}) \{ (44.22 \text{ J/mol}\cdot\text{K}) (400.0 \text{ K} - 300.0 \text{ K}) \\ + \frac{1}{2} (8.79 \times 10^{-3} \text{ J/mol}\cdot\text{K}^2)[(400.0 \text{ K})^2 - (300.0 \text{ K})^2] \\ - (-8.62 \times 10^5 \text{ J}\cdot\text{K/mol}) [(1/400.0 \text{ K}) - (1/300.0 \text{ K})] \} \\ = (5.000 \text{ mol}) [4422. \text{ J/mol} + 307.6 \text{ J/mol} - 718.3 \text{ J/mol}] = 20056. \text{ J}$$

5) a) For the calculation at $T = 25.0\text{ }^{\circ}\text{C}$ we can use the general procedure

$$\begin{aligned}\Delta H^{\circ}_{\text{rxn}} &= [\sum \Delta H^{\circ}_{\text{f}}(\text{products})] - [\sum \Delta H^{\circ}_{\text{f}}(\text{reactants})] \\ &= [2 \Delta H^{\circ}_{\text{f}}(\text{SnO}(\text{s})) + \Delta H^{\circ}_{\text{f}}(\text{O}_2(\text{g}))] - [2 \Delta H^{\circ}_{\text{f}}(\text{SnO}_2(\text{s}))] \\ &= [2(-285.8\text{ kJ/mol}) + (0.0\text{ kJ/mol})] - [2(-580.7\text{ kJ/mol})] = +589.8\text{ kJ/mol}\end{aligned}$$

b) For the calculation at $T = 100.0\text{ }^{\circ}\text{C}$ we may say

$$\Delta H^{\circ}_{\text{rxn}}(100.0\text{ }^{\circ}\text{C}) = \Delta H^{\circ}_{\text{rxn}}(25.0\text{ }^{\circ}\text{C}) + \int_{25.0^{\circ}\text{C}}^{100^{\circ}\text{C}} \Delta C_{\text{p,m}} dT$$

Where $\Delta C_{\text{p,m}} = [\sum C_{\text{p,m}}(\text{products})] - [\sum C_{\text{p,m}}(\text{reactants})]$

$$= [2(44.31\text{ J/mol}\cdot\text{K}) + (29.36\text{ J/mol}\cdot\text{K})] - [2(52.59\text{ J/mol}\cdot\text{K})] = 12.80\text{ J/mol}\cdot\text{K}$$

Since we are assuming all of the values for $C_{\text{p,m}}$ are constant over the temperature range of the problem, it follows that $\Delta C_{\text{p,m}}$ is also constant, and so therefore can be taken outside the integral. This gives

$$\begin{aligned}\Delta H^{\circ}_{\text{rxn}}(100.0\text{ }^{\circ}\text{C}) &= \Delta H^{\circ}_{\text{rxn}}(25.0\text{ }^{\circ}\text{C}) + \int_{25.0^{\circ}\text{C}}^{100^{\circ}\text{C}} \Delta C_{\text{p,m}} dT \\ &= \Delta H^{\circ}_{\text{rxn}}(25.0\text{ }^{\circ}\text{C}) + \Delta C_{\text{p,m}} (100.0\text{ }^{\circ}\text{C} - 25.0\text{ }^{\circ}\text{C}) \\ &= 589.8\text{ kJ/mol} + (12.80 \times 10^{-3}\text{ kJ/mol}\cdot\text{K})(75.0\text{ K}) = 590.8\text{ kJ/mol}\end{aligned}$$

For this particular reaction the temperature dependence of $\Delta H^{\circ}_{\text{rxn}}$ is not very important. There are many cases where the temperature dependence is sufficiently large that it needs to be taken into account.