

Department of Chemistry, Oregon State University  
Physical Chemistry Assignment 3  
due: 7 November 2014

1. Problem 3.5 (taken from Silbey, et al, 4th ed)
2. Problem 3.7
3. Problem 3.9
4. Problem 3.25
5. Problem 3.28a. Next compare the adiabatic lapse rate in K/Km with that we used in problem set 1, viz., 7 K/Km.
6. Problem 3.39
7. Problem 4.6 Present the difference as  $\frac{C_p - C_v}{R}$ .
8. Problem 4.11
9. Problem 4.15

### Problem set 3

1. 3.5

$$\Delta S(\text{water, } 100^\circ\text{C}) = \frac{40.69 \text{ kJ}}{373.15 \text{ K}} = 109.04 \frac{\text{J}}{\text{K}}$$

$\Delta S(\text{water} + \text{reservoir}) = 0$  if reversible

2. 
$$\Delta S_V = \int dT C_V / T = C_V \ln(T_2 / T_1) = C_V \ln(5/3)$$

$$\Delta S_P = C_P \ln(T_2 / T_1) = C_P \ln(5/3)$$

$$\text{with } C_V = \frac{3}{2}R, C_P = \frac{5}{2}R$$

3. 3.9

$$\Delta S = C_P \ln\left(\frac{T_{\text{final}}}{T_1}\right) + C_P \ln\left(\frac{T_f}{T_2}\right)$$

but  $T_f = \left(\frac{1}{2}\right)(T_1 + T_2)$  since

$$\Delta H = 0 = C_P(T_f - T_1) + C_P(T_f - T_2)$$

and so 
$$\Delta S = C_P \ln\left(\frac{T_f^2}{T_1 T_2}\right)$$

$$\frac{\Delta S}{C_P} = \ln\left(\frac{\left(\frac{1}{2}(T_1 + T_2)\right)^2}{T_1 T_2}\right) > 0 \quad \text{Is this greater than zero? yes}$$

$$\frac{\Delta S}{C_P} = \ln\left(\frac{1}{4}\left(2 + \frac{1}{x} + x\right)\right) \quad x = T_1 / T_2$$

greater than 1 for all  $x$ .

4. 3.25 10g of molecular  $H_2 \Rightarrow 5$  moles

a)  $\Delta S = nR \ln(V_2/V_1) = 5R \ln(3)$  reversible expansion  
 $\Delta S_{\text{sur}} = -\Delta S, \Delta S_{\text{tot}} = 0$   
 $V_1 \rightarrow 3V_1$

b) adiabatic expansion,  $\Delta S = 0$

$$\Delta S_{\text{sur}} = 0 = \Delta S_{\text{tot}}$$

5. 3.28

a)  $\Delta S = c_p \ln(T/P_0) + R \ln(P_0/P) = 0$

$$P/P_0 = \exp(-mgh/RT)$$

↑  
pressure @ ground level

$$c_p \ln(T/T_0) + R \cdot mgh/RT_0 = 0$$

$\therefore \ln(T/T_0) = -\frac{mgh}{c_p T_0}$  exponentiate this

$$T/T_0 = \exp(-mgh/(c_p T_0)) \sim 1 - \frac{mgh}{c_p T_0}$$

or  $T = T_0 - \frac{mgh}{c_p} \Rightarrow T - T_0 = -\frac{mgh}{c_p} = \Delta T$

b)  $M = 29 \text{ g/mol}, c_p = 29.1 \frac{\text{J}}{\text{K} \cdot \text{mol}} = \frac{5}{2}R,$

$$\Delta T = \frac{-29 \frac{\text{g}}{\text{mol}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} \times 9.8 \frac{\text{m}}{\text{sec}^2} \times h(\text{km}) \times \frac{1000 \text{ m}}{\text{km}}}{29.1 \frac{\text{J}}{\text{K} \cdot \text{mol}}}$$

$$= -9.8 h(\text{km}) \frac{\text{K}}{\text{km}}$$

our previous result was  $7 \frac{\text{K}}{\text{km}}$ .

6. 3.39

$$S(T) = \int_0^T dT' \frac{C_p(T')}{T'} = \text{const} \int_0^T (T')^2 dT'$$

$$S(T) = \text{const} T^3/3 = \frac{1}{3} C_p(T)$$

$$\lim_{T \rightarrow 0} S(T), C_p(T) = 0$$

7. 4.6

$$\bar{C}_p - \bar{C}_v = T \bar{V} \alpha_p^2 / \kappa_T$$

$$\alpha_p = 35.1 \times 10^{-6} \text{ K}^{-1}, \quad \kappa_T = 0.52 \times 10^{-6} \frac{1}{\text{bar}} \times \frac{1 \text{ bar}}{10^5 \text{ Pa}}$$

$$\rho = \frac{m}{V} = 7.86 \frac{\text{g}}{\text{cm}^3} \times \left( \frac{10^2 \text{ cm}}{\text{m}} \right)^3 \times \frac{1 \text{ mole}}{55.48 \text{ g}} = \frac{n}{V} = \frac{1}{V}$$

$$T = 25^\circ\text{C} = 298 \text{ K} \quad \Rightarrow$$

$$\bar{C}_p - \bar{C}_v = 0.50 \frac{\text{J}}{\text{K mole}}, \quad \frac{\bar{C}_p - \bar{C}_v}{R} = 0.060$$

$(\bar{C}_p - \bar{C}_v)/R$  much smaller than 1 (true for ideal gases)

8. 4.11

$$\bar{V} = \left( \frac{\partial G}{\partial P} \right)_T \quad \therefore \Delta G = \bar{V} \Delta P$$

$$\Delta G = \left( 1.8 \times 10^{-5} \frac{\text{m}^3}{\text{mole}} \right) 999 \text{ bar} \times \frac{10^5 \text{ Pa}}{\text{bar}}$$

$$\Delta G = 1.8 \text{ kJ/mole}$$

9. 4.15

$$T_{\text{vap}} = 111^{\circ}\text{C} + 273\text{K} = 384\text{K}$$

$$\Delta H = \frac{381.9\text{ J}}{\text{g}} \times \frac{92.1\text{ g}}{\text{mol}} = 33.33\text{ kJ/mole}$$

MW of toluene

$$\Delta E = \Delta H - \Delta(PV) = \Delta H - (\Delta n)RT$$

$$\Delta n = 1$$

$$\therefore \Delta E = \Delta H - 8315 \frac{\text{J}}{\text{K}\cdot\text{mol}} \times 384\text{K}$$

$$\Delta E = 30,138 \frac{\text{J}}{\text{mol}}$$

$$\Delta G = 0, \text{ and } \Delta S = \frac{\Delta H}{T} = 86.8\text{ J/K}\cdot\text{mol}$$

$$\Delta U = q_p - W_{\text{by}} = \Delta H - W_{\text{by}} \Rightarrow W_{\text{by}} = \Delta H - \Delta E$$

$$W_{\text{by}} = 33.33\text{ kJ} - 30,138\text{ kJ} = 3.19\text{ kJ/mole}$$