Department of Chemistry, Oregon State University
Physical Chemistry Assignment 2
due: 24 October 2014

1. Show that the following differential form,

$$df(x, y) = dx - \frac{x}{y}dy \tag{1}$$

   is inexact by integrating over the area $x = [1, 2], y = [1, 2]$ using two different paths. In the first path, integrate x and then y, whereas in the second, integrate y and then x. Next, follow the same procedure with the differential form $dg(x, y) = df(x, y)/y$ and here the result should be an exact differential.

2. Problem 2.11a, Silbey 4th ed. Express your answer as w_{on}/n using the molar densities ρ_1 and ρ_2.

3. Problem 2.13

4. Problem 2.16a Integrate along an adiabatic path.

5. Problem 2.27

6. While at the gym, you burn 240 nutritional calories during moderate excise. If all of the calories go toward the vaporization of water, (at 2400 cal/g) how many kilograms of water have you lost.

7. Problem 2.65 (Oxalic acid is $(COOH)_2$.)

8. Write $(\partial C_v/\partial V)_T$ as a second derivative of E and find its relation to $(\partial E/\partial V)_T$. Show that $(\partial C_v/\partial V)_T$ vanishes for an ideal gas.

9. Starting from

$$C_p - C_v = T\,(\partial P/\partial T)_V\,(\partial V/\partial T)_P \tag{2}$$

   prove that

$$C_p - C_v = -T\frac{[(\partial V/\partial T)_P]^2}{(\partial V/\partial P)_T} \tag{3}$$

10. Write the expressions for the total derivatives, $d\rho(T, P)$ and $dP(\rho, T)$, i.e.,

$$d\rho(T, P) = something \cdot dT + another\ something \cdot dP \tag{4}$$

   expressing the somethings in terms of α_P and κ_T.

Assignment 2

1. $$\int df = \int_{\substack{x=1\\ y=1}}^{x=2} dx - x \int_{\substack{y=1\\ x=2}}^{2} dy/y$$

$$\int = x\Big|_1^2 - 2\ln(y) = 1 - 2\ln(2)$$

path # 1

Next $$\int df = -x\int_{\substack{y=1\\ x=1}}^{2} \frac{dy}{y} + \int_{x=1}^{x=2} dx = -\ln 2 + 1$$

note the integral is path dependent

Integrate $dg = dx/y - x\,dy/y^2$

$$dg = \int_{\substack{x=1\\ y=1}}^{x=2} dx/y - x\int_{\substack{y=1\\ x=2}}^{y=2} dy/y^2 = 1 + 2\left[\frac{1}{y}\right] = 1 + 2\left(\frac{1}{2} - 1\right) = 0$$

Again,

$$dg = -x\int_{\substack{y=1\\ x=1}}^{y=2} dy/y^2 + \int_{\substack{x=1\\ y=2}}^{x=2} dx/y = x\left(\frac{1}{y}\right)\Big|_1^2 + \frac{1}{2}\cdot 1 = 0$$

∴ ~~second path~~ dg is an exact differential, whereas df is not.

2. 2.11a from Silbey

$$dE = dq_{by} + dW_{on}$$

$$W_{on} = -\int_{V_1}^{V_2} P_{ext}\, dV$$

but $P = \dfrac{nRT}{V-nb} - \dfrac{an^2}{V^2}$

$$W_{on} = -\int dV \frac{nRT}{V-nb} + an^2 \int dV/V^2$$

$$= -nRT \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) - an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$\frac{W_{on}}{n} = -RT \ln\left(\frac{\rho_1(1-b\rho_2)}{\rho_2(1-b\rho_1)}\right) - a(\rho_2 - \rho_1)$$

3 | 2.13 isothermal reversible expansion of an ideal gas.

$dU = C_v dT = dq - PdV$

$$W_{on} = -\int PdV = -nRT\int_{V_1}^{V_2} \frac{dV}{V} = -nRT\ln(V_2/V_1)$$

$$\frac{P_2}{P_1} = \frac{1\ \text{bar}}{10\ \text{bar}} = \frac{V_1}{V_2}, \quad V_2/V_1 = 10, \; T = 298.15\,K$$

$$W_{on} = -RT\ln(10) = -5.7\,kJ$$

$$\Delta U = 0 = q_{by} + W_{on} \Rightarrow q_{by} = -W_{on} = RT\ln(10) = 5.7\,kJ$$

$$\Delta U = \Delta H = 0$$

If the pressure is constant, then

$$W = -P_{ext}(V_2 - V_1) = -1\,\text{bar} \times \left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

$P_2 = 1$ bar, $P_1 = 10$ bar

$$W_{by} = -1\,\text{bar} \cdot RT\left(\frac{1}{10} - 1\right)\frac{1}{\text{bar}} = 0.9 \cdot RT = 2.23\,kJ$$

4. 2.16a

$$W_{on} = -\int_{V_1}^{V_2} P\,dV \,, \qquad P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

$$P_2 = P_1 V_1^{\gamma} / V_2^{\gamma} \quad \text{or} \quad W_{on} = -\int_{V_1}^{V_2} dV \, P_1 V_1^{\gamma} \frac{dV}{V^{\gamma}}$$

$$W_{on} = \frac{P_1 V_1^{\gamma}}{\gamma - 1} \left\{ \frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right\}$$

$$= \Big\{ P_1 V_2 \underbrace{\left(\frac{V_1}{V_2}\right)^{\gamma}}_{P_2/P_1} - P_1 V_1 \Big\} / \gamma - 1 \quad = \quad \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

5. 2.27

$$\Delta H \{ L(-10°C) \rightarrow S(-10°C) \}$$

convert to an alternative reversible path

$$\Delta H (L(-10°C) \rightarrow L(0°C))$$
$$\Delta H (L(0°C) \rightarrow S(0°C))$$
$$\Delta H (S(0°C) \rightarrow S(-10°C))$$

$$= \underbrace{C_p(L)(10K)}_{C_p \Delta T} \quad \underbrace{- 6004 J}_{+\Delta H \text{ @ } 273K} \quad \underbrace{+ C_p(S)(-10K)}_{C_p \, \Delta T}$$

$$= \left(75.3 \frac{J}{K}\right) 10K - 6004 J - (36.8)(10\ J/K)$$

$$\Delta H\,(\text{TOTAL}) = -5.62 \text{ kJ/mole}$$

6. $240 \text{ Cal} \times \frac{1 \text{ kcal}}{1 \text{ Cal}} \times \cancel{\frac{4.184 \text{ J}}{\text{cal}}} \times \frac{1 \text{ g}}{2400 \text{ cal}} = \cancel{418} \text{ g} \; 0.1 \text{kg}$

assuming no mechanical losses.

7. 2.65

$$\Delta U = -90\text{g oxalic acid} \times 2.816 \text{ kJ/g}$$

$$\Delta U = -253 \text{ kJ}$$

$$\Delta H = \Delta[U + PV] = \Delta U + (\Delta n)RT$$

$$HO-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-OH + O_2 \rightarrow CO_2 + H_2O$$

$$(COOH)_2 + \tfrac{1}{2}O_2 \rightarrow 2CO_2 + H_2O(L)$$

$$\Delta n = 2 - \tfrac{1}{2} = \tfrac{3}{2}$$

$$\Delta H = -253 \text{ kJ} + (3/2)(8.314 \tfrac{J}{K})(298 K)$$

$$= -249.7 \text{ kJ/mole}.$$

8. $C_V = (\partial E/\partial T)_V$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial E}{\partial T}\right)_V\right)_T = \frac{\partial}{\partial T}\underbrace{\left(\frac{\partial E}{\partial V}\right)_T}_{=0} = 0$$

9. $$C_p - C_V = T\underbrace{\left(\frac{\partial P}{\partial T}\right)_V}_{\text{cyclic rule } = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P}\left(\frac{\partial V}{\partial T}\right)_P$$

$$C_p - C_V = -T(\partial V/\partial T)_P^2 \Big/ (\partial P/\partial V)_T$$

10.

$$d\rho = \underbrace{\left(\frac{\partial \rho}{\partial P}\right)_T}_{\rho \kappa_T} dP + \underbrace{\left(\frac{\partial \rho}{\partial T}\right)_P}_{-\alpha_P \rho} dT = \rho\left\{\kappa_T dP - \alpha_P dT\right\}$$

$$dP = \left(\frac{\partial P}{\partial \rho}\right)_T d\rho + \left(\frac{\partial P}{\partial T}\right)_\rho dT$$

$$\left(\frac{\partial \rho}{\partial P}\right)_T = \rho \kappa_T \qquad \left(\frac{\partial P}{\partial T}\right)_\rho = -\left(\frac{\partial P}{\partial \rho}\right)_T\left(\frac{\partial \rho}{\partial T}\right)_P = -\frac{1}{\rho \kappa_T} \cdot -\alpha_P \rho$$

$$dP = \frac{d\rho}{\rho \kappa_T} + \frac{\alpha_P}{\kappa_T} dT$$

$$dP = \frac{1}{\kappa_T}\left(\frac{d\rho}{\rho} + \alpha_P dT\right)$$