

Model Answers
CY 102 – Physical Chemistry II
Quiz – I
24th February 2004

1. a) Derive the Maxwell relation $[\partial T/\partial P]_s = [\partial V/\partial S]_p$

Since $dH = dE + PdV + VdP = TdS + VdP$ is an exact differential,
 $(\partial T/\partial P)_s = (\partial V/\partial S)_p$

- b) Which of the following statements is correct? Rationalize your answer.

Two reversible adiabatic curves in the PV diagram

- i) can intersect only at one point
- ii) can intersect at more than one point
- iii) can not intersect

Ans: If $r(C_p/c_v)$ is same, they can not intersect, since there is only one unique adiabatic curve satisfying $P_1V_1^r = P_2V_2^r$ (2)

r is different, they can intersect at one point (2)

For Ans (ii) no marks

- c) Determine the maximum number of phases that can coexist in the following cases:

i) Ag – Pb alloy investigated at constant pressure $P_{\max} = 3$ $P + F = C + 1$

ii) $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$; $P_{\max} = 3$

iii) $\text{NH}_4\text{Cl}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{HCl}(\text{g})$; $P_{\max} = 2$

2. Fill up the blanks from the choices given below:

i) $dS \geq \delta q/T$ ii) $dS \leq \delta q/T$ iii) Water iv) Benzene v) dF (or dA) > 0 ;
vi) dF (or dA) < 0 ; vii) $dG < 0$; viii) 12R ix) 13 R x) Positive; xi) Negative

a) Clausius inequality is represented as $dS \geq \delta q/T$

b) Trouton's rule is not obeyed in the case of Water

c) The condition for spontaneity in the case of a system at constant temperature and volume is $dF < 0$

d) The theoretically expected value for C_v in the case of $\text{CH}_4(\text{g})$ is 12 R at 298K.

e) $\partial P/\partial T$ for $\text{H}_2\text{O}(\text{s})$ in equilibrium with $\text{H}_2\text{O}(\text{l})$ is negative

3. The sublimation pressure of a compound is 1012.3 mm. Hg at 193K and 449.3 mm. Hg at 183K. Calculate the enthalpy of sublimation and the sublimation temperature at one atm pressure.

$$\ln P_2/P_1 = \Delta H^0 (T_2 - T_1)/R T_1 T_2$$

After substituting, $\Delta H^0/R \approx 2868.61$

$$\therefore \Delta H^0 \approx 23.85 \text{ kJ/mol}$$

$$\ln(1012.3/760) = 2868.61 (193 - T_1)/193 T_1$$

$$T_1 \approx 189.3 \text{ k}$$

If the other data is used also, the same temp. is obtained.

4. From the following data



evaluate the minimum temperature above which the reduction of MnO by C is possible.

More than 1689.2 K

5. An ideal Carnot heat engine operates on a temperature difference of 210 degrees. One third of the heat absorbed from the source is discharged to the sink. If the work done per cycle is 400 J, calculate T_1 , T_2 , q_1 , q_2 and η .

$$\text{Ans: } q_1 + q_2 = 400 \text{ J since } \oint dE = 0$$

$$q_1 = \text{Heat absorbed from the source; } q_2 = -q_1/3$$

$$\therefore q_1 - q_1/3 = 400; q_1 = 600 \text{ J; } q_2 = -200 \text{ J.}$$

$$\eta = W/Q_1 = 400 \text{ J}/600 \text{ J} = 2/3 = T_2 - T_1/T_2 = 210/T_2$$

$$\therefore T_2 = 315 \text{ k; } T_1 = 105 \text{ k.}$$

6. A mixture of an organic compound (molecular weight is 114) and water boils at 90°C at a constant pressure of 732 mm Hg. The vapour pressure of water is 528 mm Hg. Calculate the mass of steam required to distill 500 gms of the organic compound.

$$P_e/p_w = W_e/M_e / W_w / M_w$$

$$204/528 = 500 \times 18 / 114 \times W_w$$

$$\therefore W_w \approx 204.33 \text{ gm.}$$

7. One mole of an ideal monatomic gas at 300 K is allowed to expand isothermally and reversibly from an initial pressure of 15 atm to a final pressure of 1 atm. Calculate W , ΔG , ΔH and ΔS .
 $\Delta H = 0$.

$$\Delta G = RT \ln P_2/P_1 = -812.415 R \approx -6754.41 \text{ J}$$

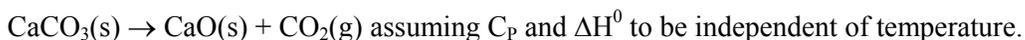
$$W = RT \ln P_1/P_2 = 6754.41 \text{ J}$$

$$\Delta S = R \ln P_1/P_2 = 2.708 R \approx 22.515 \text{ Jk}^{-1}\text{mol}^{-1}$$

8. From the following data

Compound	ΔH_{298}^0 (kJ mol ⁻¹)	S_{298}^0 (J K ⁻¹ mol ⁻¹)	C_p (JK ⁻¹ mol ⁻¹)
CaCO ₃ (s)	-1211.0	92.90	19.68
CaO(s)	-635.1	39.75	10.10
CO ₂ (g)	-313.5	213.60	6.40

Evaluate ΔG at 500 K, for the reaction.



I method:

$$\Delta S_{298}^0 = 39.75 + 213.60 - 92.90$$

$$= 160.45 \text{ Jk}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{500}^0 = \Delta S_{298}^0 + \Delta C_p \ln T_2/T_1 = 160.45 + (-3.18) (.5178) = 158.8 \text{ Jk}$$

$$\Delta H_{298}^0 = -635.1 - 313.5 + 1211.0$$

$$= 262.4 \text{ kJ mol}^{-1}.$$

$$\Delta H_{500}^0 = \Delta H_{298}^0 + \Delta C_p (T_2 - T_1)$$

$$= 262.4 \times 1000 + (-3.18) (202)$$

$$= 261.8 \text{ kJ mn}^{-1}$$

$$\Delta G_{500}^0 = 261.8 - 500 \times 10^{-3} \times 158.80$$

$$= 182.4 \text{ kJ mol}^{-1}.$$

9. The freezing point of a compound A is 276°C while that of a compound B is 345°C . From the following data, draw the phase diagram schematically.

Mole fraction of B	0.2	0.4	0.6	0.8
Freezing point $^{\circ}\text{C}$	253.0	145.0	225.0	323

Label various regions of the phase diagram and indicate the degrees of freedom in each region.

