Q&A
EP

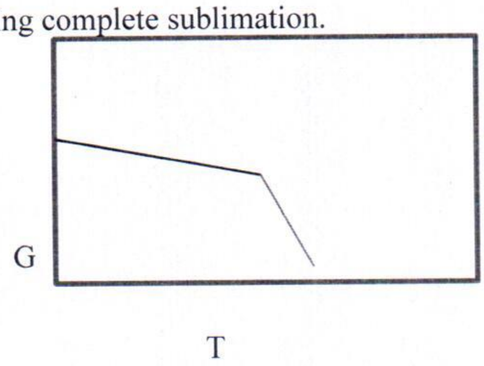
Department of Chemistry
IIT Madras
CY 1001 Mid-Semester Examination
Physical Chemistry

One mark

1. The expression for the half-life for a zero order reaction is $\boxed{t_{1/2} = \frac{[A]_0}{2k}}$
2. The overall rate constant of a composite reaction involving two elementary steps with rate constants k_1 and k_2 is given by $k_{overall} = \frac{k_1}{k_2}$. If E_1 and E_2 are the activation energies of the individual steps, $E_{overall} = E_1 - E_2$

Two marks

3. Plot a graph, showing the variation in Gibbs energy, G, with temperature T, for a pure solid undergoing complete sublimation.



4. What is the temperature of a two level system of energy separation equivalent to 300 cm^{-1} when population of the upper state is one half of the lower state?

$$\frac{n_2}{n_1} = e^{-\frac{(\varepsilon_2 - \varepsilon_1)}{kT}}$$

e2-e1 = 300 cm^{-1}
n2/n1 = 0.5

Substituting this in the above equation, T = 623 K.

Three marks

5. The frequency factor for an apparently unimolecular reaction at 473 K is 2.5 x 10^{18} s^{-1}. Calculate entropy of activation, $\Delta S^{0\ddagger}$.

$$A = \frac{RT}{N_a h} \exp\left(\Delta S^{0\mp} / R\right) \exp\left(1 - \Delta n^{\mp}\right)$$

$$\Rightarrow \exp\left(\frac{\Delta S^{0\mp}}{R}\right) = A\left(\frac{N_a h}{RT}\right) e^{-1}$$

$$\frac{\Delta S^{0\mp}}{R} = \ln\left(\frac{A N_a h}{RT}\right) - 1$$

$$\Delta S^{0\mp} = \ln\left\{\frac{\left(2.5\times10^{13}\right)\left(6.022\times10^{-34}\right)}{8.314\times473}\right\} - 8.314$$

$= 7.742\ Jk^{-1}\ mol^{-1} - 8.314\ JK^{-1} mol^{-1} = -0.572\ Jk^{-1}$

Four marks

6. The Arrhenius parameters for the thermal decomposition of NOCl represented by, $2NOCl\ (g) \rightarrow 2NO\ (g) + Cl_2\ (g)$ are $A = 1.00 \times 10^{13}\ M^{-1}\ s^{-1}$ and $E_a = 104\ kJ\ mol^{-1}$. Calculate the entropy ($\Delta^{\#}S$), enthalpy ($\Delta^{\#}H$) and free energy ($\Delta^{\#}G$) of activation for the reaction at 300K.

$$k = Ae^{-E_a/RT}$$

$$\Rightarrow E_a = RT^2 \frac{d\ln k}{dT} \quad (1)$$

From TST

$$k = \frac{k_B T}{h}\left(\frac{RT}{P^0}\right)K_P \qquad \text{substitute } K \text{ by } e^{\Delta S/R} e^{-\Delta H/RT} \text{ take } \ln k \text{ and diffrentiate wrt } T$$

$$\Rightarrow \frac{d\ln k}{dT} = \frac{2}{T} + \frac{\Delta H}{RT^2} \qquad (2) \quad \text{comparing (1) and (2)}$$

$$\Rightarrow E_a = \Delta H + 2RT$$

$$\Delta H^{\#} = E_a - 2RT = 104 kJ\, mol^{-1} - 2(8.314\, J\, K^{-1}\, mol^{-1})(300K)$$

$$\Rightarrow \Delta H^{\#} = 99.0 kJ\, mol^{-1}$$

$$\Delta S^{\#} = R\ln\left(\frac{Ahc}{e^2 k_B T}\right)$$

$$\Rightarrow \Delta S^{\#} = (8.314\, J\, K^{-1}\, mol^{-1})\ln\left(\frac{(1.00\times10^{13}\, M^{-1}s^{-1})(6.626\times10^{-34}\, Js)(1M)}{e^2(1.38\times10^{-23}\, JK^{-1})(300K)}\right)$$

$$\Rightarrow \Delta S^{\#} = -12.7\, J\, K^{-1}\, mol^{-1}$$

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

$$\Rightarrow \Delta G^{\#} = 99.0 kJ\, mol^{-1} - (300K)\times(-12.7\, J\, K^{-1}\, mol^{-1})$$

$$\Rightarrow \Delta G^{\#} = 102.8 kJ\, mol^{-1}$$

Sec: I

CY 1001 Model Answers ✓ RD/EP/TP/PS

Mid-Sem March 2015

1 + (or) positive

2 $-(\partial V/\partial T)_p = (\partial \boxed{S}/\partial p)_T$. Answer is S

3 H

4 $dp/dT = \Delta S/\Delta V$. Answer is ΔV.

5 Q

6 $c_0/2k$ (or) $A_0/2k$ (or) $a/2k$ (or) initial concentration/2k.

7 E_a (overall) $= E_1 - E_2$

8 First and second

9 $k = k_2 K_{eq}$

10 number of molecules of substrate turned into products per (active site) enzyme molecule, per second.

11. $y = 0$

12. Q

Sec: II Question 13 (2 marks each)

$$T_m = \underset{\substack{\downarrow \\ \text{1 mark.}}}{\frac{\Delta H^\ominus}{\Delta S^\ominus}} = \frac{13100}{7} = \underset{\substack{\downarrow \\ \text{1 mark.}}}{1871.4\ \text{K.}}$$

Question 14

$$Al_2O_3 + 3C \longrightarrow 2Al + 3CO \leftarrow \boxed{\text{1 mark.}}$$

$$\Delta G^\ominus_{r} = 3\Delta G^\ominus_f(CO) - \Delta G^\ominus_f(Al_2O_3) = +3(-190) - (-1290)$$

$$= -570 + 1290 = \boxed{+720\ \text{kJ mol}^{-1}} \leftarrow \boxed{\text{1 mark}}$$

No.

Section III Question 20 (3 marks)

For a van der Waals gas

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = RT \quad \text{———} \quad \boxed{1 \text{ mark}}$$

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

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\partial P/\partial T\right)_V - p \quad \text{———} \quad \boxed{1 \text{ mark}}$$

$$= T\left[\frac{\partial}{\partial T}\left\{\frac{nRT}{(V-nb)} - \frac{an^2}{V^2}\right\}\right] - \left[\frac{nRT}{(V-nb)} - \frac{an^2}{V^2}\right]$$

$$= T\left[\frac{nR}{(V-nb)}\right] - \left[\frac{nRT}{(V-nb)} - \frac{an^2}{V^2}\right]$$

$$= a\frac{n^2}{V^2} \text{ (or) } \pi_T \quad \text{———} \quad \boxed{1 \text{ mark}}$$

Section III Question 22 (3 marks)

$$\Delta G^{\ominus}_{g} = -2865000 - (273+38)\,182\cdot4$$

$$= -2921726\cdot4 \xrightarrow{} \boxed{1\ \text{mark}}$$

is the free energy available per mole (180 g) of glucose upon metabolism.

Energy required for 24 h of heart beat $= \underset{h}{24} \times \underset{\frac{min}{h}}{60} \times \underset{\frac{beats}{min}}{70} \times \underset{\frac{J}{beat}}{1} = 100800$ Joules $\rightarrow \boxed{1\ \text{mark}}$

$$= \frac{2921726\cdot4}{180} \times x\ \text{g} = 100800$$

$$\therefore x = 6\cdot2\ \text{g} \longrightarrow \boxed{1\ \text{mark}}$$

of glucose.

Section III Q. 25 (3 marks each)

$$\{p, q, r, s\} = \{4, 8, 12, 16\} \quad \boxed{1\ \text{mark}}$$

$$W = \frac{N!}{n_1!\, n_2!\, n_3!\, n_4!} = \frac{40!}{4!\, 8!\, 12!\, 16!} \quad \boxed{1\ \text{mark}}$$

$$= \frac{\cancel{1\times2\times3\times4\times5\times6\times7\times8\times9\times10\times11\times12\times13\times14\times15\times16} \times 17 \times \overset{3}{\cancel{18}} \times 19 \times \overset{10}{\cancel{20}} \times \overset{3}{\cancel{21}} \times 22 \times 23 \times \overset{3}{\cancel{24}} \times \overset{5}{\cancel{25}} \times 26 \times \overset{3}{\cancel{27}} \times \overset{7}{\cancel{28}} \times 29 \times \overset{5}{\cancel{30}} \times 31 \times \overset{4}{\cancel{32}} \times \overset{3}{\cancel{33}} \times \underset{17}{\cancel{34}} \times \overset{5}{\cancel{35}} \times \overset{3}{\cancel{36}} \times 37 \times \underset{19}{\cancel{38}} \times \overset{13}{\cancel{39}} \times \overset{4}{\cancel{40}}}{\cancel{16!}\ 1 \times \cancel{2} \times 3 \times \cancel{4} \times \cancel{5} \times \cancel{6} \times \cancel{7} \times \cancel{8} \times \cancel{9} \times \cancel{10} \times \cancel{11} \times \cancel{12} \times \cancel{1} \times \cancel{2} \times \cancel{3} \times \cancel{4} \times \cancel{5} \times \cancel{6} \times \cancel{7} \times \cancel{8} \times 1 \times \cancel{2} \times \cancel{3} \times \cancel{4}}$$

$$= 17 \times 3 \times 19 \times 10 \times 3 \times 22 \times 23 \times 3 \times 5 \times 26 \times 3 \times 7 \times 29 \times 31 \times 17 \times 5 \times 37 \times 19 \times 13$$

$$W = 8.4 \times 10^{19} \longrightarrow \boxed{1\ \text{mark}}$$

Note: Below 50!, Stirling's approximation is not accurate.

If they apply Stirling's approximation only ½ mark if the answer is 1.9×10^{22}

$$\ln W = (N \ln N - N) - \left[(n_1 \ln n_1 - n_1) + (n_2 \ln n_2 - n_2) + (n_3 \ln n_3 - n_3) + (n_4 \ln n_4 - n_4)\right]$$

$$= (40 \ln 40 - 40) - \left[16 \ln 16 + 12 \ln 12 + 8 \ln 8 + 4 \ln 4 - (16 + 12 + 8 + 4)\right]$$

$$= 40 \ln 40 - \left[16 \ln 16 + 12 \ln 12 + 8 \ln 8 + 4 \ln 4\right]$$

$$= 147.6 - [44.4 + 29.8 + 16.6 + 5.5] = 51.3$$

$W = \boxed{1.9 \times 10^{22}} \rightarrow$ only ½ mark

Section IV Q. 29

4 marks

[ATP] in 10^{-6} mol dm^{-3}	0.6	0.8	1.4	2	3
rate in 10^{-6} mol dm^{3} s^{-1}	0.81	0.97	1.3	1.47	1.69
$1/[S]$ mol^{-1} dm^{3} in 10^{6}	1.67	1.25	0.71	0.5	0.33
$1/rate$ in mol^{-1} dm^{-3} s	1.25	1.03	0.77	0.68	0.59

Slope of $\frac{1}{rate}$ versus $\frac{1}{[S]}$ $\Rightarrow$ slope $= \frac{K_m}{V_{max}}$

Slope $= \frac{y_2 - y_1}{x_2 - x_1}$

$$\underbrace{0.53 \quad 0.49 \quad 0.42 \quad 0.53}_{0.49 \text{ Average}}$$

$\boxed{1 \text{ mark}}$ for any one value of slope from 0.42 to 0.53

Take any one value of 1/rate

$$1.03 = 0.49 * 1.25 + 1/V_{max} \Rightarrow V_{max} = \frac{1}{0.42} = 2.38$$

$V_{max} = 2.38 * 10^{-6}$ mol dm^{3} s^{-1} — $\boxed{1 \text{ mark}}$

$\frac{K_M}{V_{max}} = 0.49 \Rightarrow K_M = 1.17 * 10^{-6}$ mol dm^{-3} — $\boxed{1 \text{ mark}}$

$V_{max} = k_2[E]_0 \Rightarrow k_2 = TON = \frac{2.38 \times 10^{-6}}{20 \times 10^{-9}} = 119\ s^{-1}$ ✓ $\boxed{1 \text{ mark}}$

Section IV   Q.30   4 marks

$\boxed{\text{1 mark}}$

Process 1 ; $W_1 = \frac{1}{2}(2\times10^3 + 1\times10^3)(5-3) = -3\text{ kJ}$

Pressure drop and volume increase. Temperature drops. So U decreases and sign of W_1 is -ve.

Process 2 ; $\Delta V = 0 \Rightarrow W_2 = 0 \longrightarrow \boxed{\text{1 mark}}$

Process 3 ; $W_3 = 2\times10^3(3-5) = +4\text{ kJ} \longrightarrow \boxed{\text{1 mark}}$

cooling under constant pressure

internal energy of the system decreases

$W_{total} = W_1 + W_2 + W_3 = -3+0+4 = 1\text{ kJ}$

∴ the system is restored to its initial state.

$\therefore \Delta U = 0 \Rightarrow W_{total} = q_{total} \Big\} \boxed{\text{1 mark}}$

$\therefore q_{total} = -1\text{ kJ}$ (heat transfer)

If $\Delta U = 0$ is written then $\frac{1}{2}$ mark may be given.

Note: 3 marks for work with 1 mark each for W_1, W_2 and W_3

only 1 mark for heat transfer (q)

Section IV Q. 31 (4 marks)

$$NO(g) + O_2(g) \xrightarrow{k_1} NO_2(g) \text{ fast}$$

$$NO_2(g) + h\nu \xrightarrow{k_2} NO(g) + O(g) \text{ fast}$$

$$O_2(g) + O(g) \xrightarrow{k_3} O_3 \text{ (slow)}$$

Balancing the equation, $NO(g) + \frac{1}{2} O_2(g) \xrightarrow{k_1} NO_2(g)$ $\boxed{\frac{1}{2} \text{ mark}}$

$$\text{Rate} = k_3 [O_2][O] \quad \boxed{\frac{1}{2} \text{ mark}}$$

Applying SSA to [O]

$$k_2 [NO_2] - k_3 [O_2][O] = 0 \Rightarrow [O] = \frac{k_2 [NO_2]}{k_3 [O_2]} \quad \boxed{\text{1 mark}}$$

Applying SSA to $[NO_2]$

$$k_1 [NO][O_2]^{1/2} - k_2 [NO_2] = 0 \qquad [NO_2] = \frac{k_1 [NO][O_2]^{1/2}}{k_2} \quad \boxed{\text{1 mark}}$$

$$\therefore \frac{d[O_3]}{dt} = \cancel{k_3}\,\cancel{[O_2]}\left(\frac{\cancel{k_2}}{\cancel{k_3}}\right)\frac{1}{\cancel{[O_2]}} \times \frac{k_1 [NO][O_2]^{1/2}}{\cancel{k_2}}$$

$$= k_1 [NO][O_2]^{1/2} \quad \boxed{\text{1 mark}}$$

If the first reaction is not balanced then 1 mark may be subtracted/need not be given ($\frac{1}{2}$ mark for not balancing; $\frac{1}{2}$ mark for deriving properly, with the unbalanced equation.

PS

Q.16

$$E_a = \frac{0.693 \times 8.314 \times 300 \times 290}{10}$$

$$= 50.1 \text{ kJ mol}^{-1} \quad — ①$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{T_2 - T_1}{T_1 \times T_2}\right) \quad — ①$$

②

Q.18

$$Q = \frac{K[A]}{1+K[A]}$$

a) $$0.75 = \frac{P \times 1\ \text{bar}^{-1}}{1+(P\times 1)\ \text{bar}^{-1}}$$

$$= \frac{P}{1+P}$$

$$= 3\ \text{bar} \quad \text{——} ①$$

b) $$Q = \frac{1000}{1+1000}$$

$$= 0.999 \quad \text{——} ②$$

Q. 21

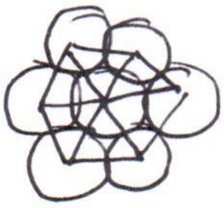
Sq. latt. $\frac{\pi R^2}{(2R)^2} = 0.785$ or 78.5% ①

Tri. latt. $\frac{\pi R^2}{2\sqrt{3}\,R^2} = 0.907$ or 90.7% $\frac{②}{②}$

$$\frac{n \times \text{Area of circle}}{\text{Area of Square}} = 78.5\% \quad \frac{\left(4\times\frac{1}{4}\right)\pi R^2}{(2R)^2}$$

$$\frac{n \times \text{Area of circle}}{\text{Area of } \text{~~Rectangle~~ Triangle}} = 90.7\%$$

$$= \frac{\left(3\times\frac{1}{6}\right)\pi R^2}{\frac{\sqrt{3}}{4}(2R^2)}$$



Q 24

$k_1 = e^{-\Delta G_1^0/RT}$

$= 1.6 \times 10^{-3}$ — ①

$P + Q \overset{k_3}{=} B + C$

$\Delta G_3^0 = 16 - 20 = 4$ kJ

$k_3 = 4.97$ — ①

Preferred Product B + C — ①

③

Q.27

For the reaction, 2 NO_2 (g) + F_2 (g) → 2 NO_2F (g), the rate law is, *rate* = k [NO_2] [F_2] .

Can the elementary reaction be the same as the overall reaction? Explain.

The rate determining step is the slowest elementary step in a mechanism, and the rate law for this step is the rate law for the overall reaction.

The (determined) rate law is,

rate = k [NO_2] [F_2], for the reaction,

2 NO_2 (g) + F_2 (g) → 2 NO_2F (g),
and a two-step mechanism is proposed:

1) NO_2 (g) + F_2 (g) → NO_2F (g) + F (g) — ①
2) NO_2 (g) + F (g) → NO_2F (g) — ①

The rate for step 1) is rate = *k* [NO_2] [F_2], which is the rate law, this suggests that step 1) is the rate-determining or the slow step. — ①

③

26 A certain solid sample adsorbs 0.84 mg of CO, when the pressure of the gas is 36 kPa and the temperature is 300 K. If the cross sectional area of CO molecule is 1×10^{-16} cm^2, then what is the surface area of the material, if the adsorption is described by Langmuir isotherm.

Ans.

Langmuir isotherm is $\theta = Kp/(1 + Kp)$

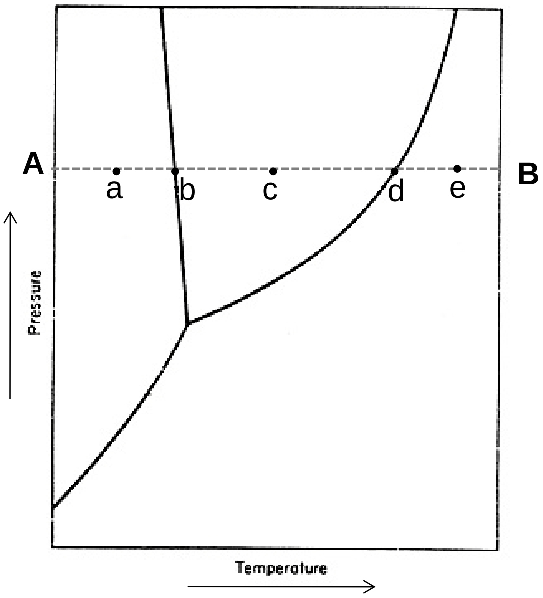
Since it obeys Langmuir isotherm, it forms one monolayer at 36 kPa.

As per the Langmuir model, the gas adsorbed forms a monolayer, 0.84 mg of CO form one monolayer on the material.

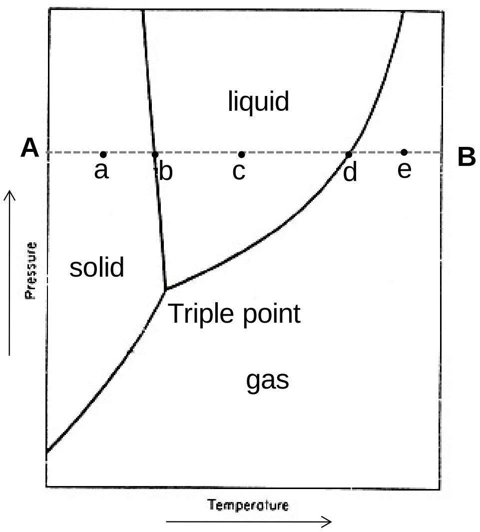
Number of molecules in one monolayer $=(0.00084/28) \times 6.023\times10^{23} = 1.8 \times 10^{19}$ molecules

One molecule is having a cross sectional area of 1×10^{-16} cm^2 so the total surface area of monolayer is 1×10^{-16} $cm^2 \times 1.8 \times 10^{19} = 1.8 \times10^{3}$ cm^2

4. Label the regions (solid, liquid or gas) of the phase diagram of a one component system given below. Find out the degrees of freedom at the specific points mentioned, across the line AB.



Ans:



Here, number of components is 1,
So, degrees of freedom at points A, a, c, e and B,
F= C- P + 2 = 1-1+2 = 2
At points b and d,
F = 1-2+2 = 1

Or a question to draw a simple eutectic system.