

DEPARTMENT OF CHEMISTRY, IIT MADRAS
CY 101: PART-B: EQUILIBRIUM AND DYNAMICS OF CHEMICAL SYSTEMS
I B. Tech. End Semester Examination; November 26, 2007
Marks: 60 (this part); Time: 3 hours (Part A+ Part B)

Use a separate answer book for this part. Write the following on the answer book:

“PART-B: EQUILIBRIUM AND DYNAMICS”

BATCH: _____ ROLL NO: _____

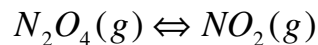
NAME: _____

$R = (8.3145 \text{ J} = 0.0821 \text{ atm dm}^3) \text{ K}^{-1} \text{ mol}^{-1}$, $k_B = 1.38 \times 10^{-23} \text{ J/K}$, $h = 6.626 \times 10^{-34} \text{ Js}$, $1 \text{ Torr} = 133.3 \text{ Pa}$

For questions 1 to 20, please answer “True” or “False”. Each question carries one mark.

1. The slope of a graph in which the reactant concentration in y-axis is plotted versus time in x-axis is positive for a zero order reaction. False
2. All chemical reactions involving surfaces require adsorption. False
3. The fastest elementary step in a complex reaction scheme controls the rate of the overall reaction. False
4. The rate of an irreversible chemical reaction can be affected by removing some products. False
5. For a second order reaction $A + B \rightarrow \text{products}$, when $[A]_0$ is reduced by a factor of 2, the half life doubles. True
6. Langmuir adsorption isotherm reduces to, $\theta = kP^n$ (where k is a constant and n is between 0 and 1, also called the Freundlich adsorption isotherm) at the limit of high pressures. False
7. As the ΔG^0 for a reaction changes from a large negative to a large positive value, K of the reaction will change from a large positive to a large negative value. False
8. K_p for the reaction $C(g) + CO_2(g) \rightarrow 2CO(g)$ will change by raising the temperature. True
9. Adsorption has an activation barrier. True
10. A unimolecular reaction shows first order kinetics at high pressures. True
11. Number of adsorption sites on a surface is the number of substrate atoms exposed. False

12. There are 2 degrees of freedom for the following system.



True

13. Chemisorption generally increases with increasing temperature till a critical value.

True

14. In collision theory, the pre-exponential factor is a measure of the rate at which collisions occur in the gas.

True

15. Multilayer adsorption is generally physisorption.

True

16. For a reaction $A + B \rightarrow products$, if $[A] \gg [B]$, the reactant with lower concentration determines the order of the reaction.

True

17. In a microcanonical ensemble the energy of the system can fluctuate.

False

18. When a system undergoes spontaneous change at constant T and P, the Gibbs energy decreases until equilibrium is reached.

True

19. The rate of an enzyme catalyzed reaction will be exactly half of the maximum rate, when $[substrate] = \text{Michaelis constant}$.

True

20. The steady state method is based on the fact that the concentration of the intermediate may change significantly during a reaction, after the initial buildup.

False

Answer all the following questions.

21. The vapor pressure of benzene between 10 °C and 30 °C fits the expression

$$\log(p/Torr) = 7.960 - \frac{1780(K)}{T}. \text{ Calculate the enthalpy of vaporization. 3 marks}$$

Ans:

21.

$$\log p = 7.960 - 1780/T \quad (\text{given}) \quad (1)$$

$$\log p = \text{constant} - \frac{\Delta_{vap}H}{2.303RT} \quad (2)$$

Comparing (1) and (2)

$$\begin{aligned} \Delta_{vap}H &= 2.303 \times 1780K \times 8.314 JK^{-1}mol^{-1} \\ &= 34.08 KJmol^{-1} \end{aligned}$$

22. The molar Gibbs energy of a certain gas is given by $G_m = RT \ln p + A + Bp + \frac{Cp^2}{2} + \frac{Dp^3}{3}$,

where A, B, C and D are constants and p is pressure. Obtain the equation of the state of gas. **4 marks**

Ans:

22. The equation of state connects V_m, T and p . From fundamental equation

$$\begin{aligned} dG_m &= -S_m dT + V_m dp \\ \left(\frac{\partial G_m}{\partial p}\right)_T &= V_m \\ \left(\frac{\partial G_m}{\partial p}\right)_T &= \frac{RT}{p} + B + Cp + Dp^2 \end{aligned}$$

Comparing the above two equations, the equation of state is given by

$$V_m = \frac{RT}{p} + B + Cp + Dp^2$$

23. The enzyme catalyzed conversion of a substrate at 25 °C has a Michaelis constant of 0.035 M. The rate of the reaction is $1.15 \times 10^{-3} \text{ M s}^{-1}$ when the substrate concentration is 0.110 M. What is the maximum velocity of this enzymolysis? **4 marks**

Ans:

Maximum velocity = $k_b[E]_0$

$$\frac{dp}{dt} = k[E]_0$$

$$k = \frac{k_b[S]}{K_M + [S]}$$

$$v = \frac{k_b[S][E]_0}{K_M + [S]}$$

$$\begin{aligned} k_b[E]_0 &= \left(\frac{K_M + [S]}{[S]}\right) v = \frac{0.035 + 0.110}{0.110} \times 1.15 \times 10^{-3} \\ &= 1.52 \times 10^{-3} \text{ M s}^{-1} \end{aligned}$$

24. In the stratosphere, the key reaction for the O_3 dissociation is $Cl + O_3 \xrightarrow{k} ClO + O_2$

The rate coefficient for this reaction is reported to be $k = (1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}) e^{-260K/T}$

- (a) What is the rate of this reaction at 20 km altitude where, $[Cl] = 5 \times 10^{-17} \text{ M}$, $[O_3] = 8 \times 10^{-9} \text{ M}$ and $T = 220 \text{ K}$?
- (b) What should be the temperature of the stratosphere at 45 Km altitude, if the rate of reaction is $1.56 \times 10^{-15} \text{ M s}^{-1}$, when $[Cl] = 3 \times 10^{-15} \text{ M}$, and $[O_3] = 8 \times 10^{-11} \text{ M}$?

(Hint: Altitudes are given to substantiate the data. They are not the part of the calculations.)

4 marks

Ans:

$$\text{Rate} = k \times [Cl][O_3]$$

$$\text{Rate} = 1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} e^{-\frac{260K}{T}} \times [Cl][O_3]$$

$$(a) \text{Rate}_{220K} =$$

$$1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} e^{-\frac{260K}{220K}} \times [5 \times 10^{-17} \text{ M}][8 \times 10^{-9} \text{ M}]$$

$$\text{Rate}_{220K} = 2.08 \times 10^{-15} \text{ Ms}^{-1}$$

$$(b) 1.56 \times 10^{-15} \text{ Ms}^{-1} =$$

$$1.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} e^{-\frac{260K}{T}} \times [3 \times 10^{-15} \text{ M}][8 \times 10^{-11} \text{ M}]$$

$$\Rightarrow T = 270 \text{ K}$$

25. For the sequential reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ the rate constants are $k_1 = 5 \times 10^6 \text{ s}^{-1}$ and $k_2 = 3 \times 10^6 \text{ s}^{-1}$. Determine the time at which concentration of $[B]$ is maximum.

$$\text{where, } [B]_t = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

4 marks

Ans:

To find t_{\max} one needs to differentiate $[B]_t$ w. r. t time and equate it to zero.

$$\frac{d[B]_t}{dt} = 0 = \frac{k_1[A]_0}{(k_2 - k_1)} [-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}]$$

$$\Rightarrow k_1 e^{-k_1 t} = k_2 e^{-k_2 t} \Rightarrow \ln\left(\frac{k_1}{k_2}\right) t_{\max}$$

$$\Rightarrow t_{\max} = \frac{1}{(k_1 - k_2)} \ln\left(\frac{k_1}{k_2}\right)$$

$$\Rightarrow t_{\max} = \frac{1}{(5-3) \times 10^6 \text{ s}^{-1}} \ln\left(\frac{5 \times 10^6 \text{ s}^{-1}}{3 \times 10^6 \text{ s}^{-1}}\right) = 2.55 \times 10^{-7} \text{ s}$$

26. Calculate the number of oxygen molecules striking 1 cm^2 of a surface in 1sec at the pressure and temperature of 10^{-6} Torr and 298K, respectively. Given that the surface of an atomic solid has about 10^{15} atoms/cm² and assuming that every oxygen molecule that strikes sticks, calculate the fraction of the surface covered.

4 marks

Ans:

$$\text{Number of molecules striking} = \frac{PN}{\sqrt{2\pi MRT}}$$

Substituting the values, we get the answer as $3.60 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$

$$\text{Given sites per cm}^2 = 10^{15}$$

Therefore, the fraction of surface covered $= 3.60 \times 10^{14} / 10^{15} = 0.36$ (36%) at 298 K

27. N independent particles exist in one of the 3 non-degenerate energy levels of energies $-E, 0, +E$. The system is in contact with a thermal reservoir at temperature T.

- What is the entropy of the system at $T=0$?
- What is the maximum possible entropy of the system?
- What is the minimum possible energy of the system?
- What is the partition function of the system?
- If $C(T)$ is the heat capacity of the system, what is the value of

$$\int_0^{\infty} \frac{C(T)}{T} dT ?$$

5 marks

Ans:

$$(a) S(0) = 0$$

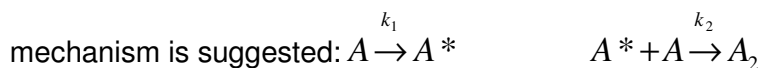
$$(b) S_{max} = Nk \ln 3$$

$$(c) E_{min} = -NE$$

$$(d) Q = q^N = (1 + e^{E/kT} + e^{-E/kT})^N$$

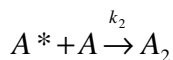
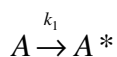
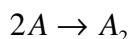
$$(e) \int_0^{\infty} \frac{C(T)}{T} dT = \int_0^{\infty} ds = S(\infty) - S(0) = Nk \ln 3$$

28. A dimerization $2A \rightarrow A_2$ is found to be first order, with a half life of 666s. The following



where $k_2 \gg k_1$. (a) What is the value for the rate constant k_1 ? (b) What is the rate law representing the overall reaction? (c) If the initial concentration of A is 0.05M, how much time is required to reach $[A] = 0.0125 \text{ M}$? **6 marks**

Ans: $k_1 = 5.20 \times 10^{-4} \text{ s}^{-1}$ time = 1333 s



$$(a) t_{1/2} = 666 = \frac{0.693}{k} \Rightarrow k = 1.04 \times 10^{-3} \text{ s}^{-1}$$

but $k_1 = \frac{k}{2} \Rightarrow k_1 = 5.20 \times 10^{-4} \text{ s}^{-1}$ (*k is the overall rate constant. they have to work out question (b) to find this relation*)

(b) Applying steady state approximation

$$\frac{dA^*}{dt} = 0 = k_1[A] - k_2[A^*][A]$$

$$k_2[A^*] = k_1$$

$$[A^*] = \frac{k_1}{k_2}$$

$$\text{rate} = \frac{1}{2} \frac{d[A]}{dt} = k_2[A^*][A] = k_1[A]$$

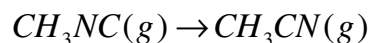
$$\text{rate} = 2k_1[A] = k[A] \quad \left\{ \Rightarrow k_1 = \frac{k}{2} \right\}$$

$$(c) \ln \frac{[A]_0}{[A]} = kt$$

$$\ln \frac{0.05}{0.0125} = 1.04 \times 10^{-3} t$$

$$\Rightarrow t = \frac{1.38}{1.04 \times 10^{-3}} = 1.33 \times 10^3 \text{ s}$$

29. Consider the “Unimolecular” isomerization of methylisocyanide,



The Arrhenius parameters are $A = 2.5 \times 10^{16} \text{ s}^{-1}$ and $E_a = 272 \text{ kJ mol}^{-1}$. Compute the Eyring parameters ΔH^\ddagger and ΔS^\ddagger for this reaction with $T = 300\text{K}$. **6 marks**

Ans:

This is a unimolecular reaction.

$$\Delta H^\ddagger = E_a - RT = 272000 \text{ J mol}^{-1} - (8.314 \text{ J K}^{-1} \text{ mol}^{-1})(300\text{K})$$

$$\Rightarrow \Delta H^\ddagger = 269505 \text{ J mol}^{-1} = 269.5 \text{ kJ mol}^{-1}$$

$$\Delta S^\ddagger = R \ln \left(\frac{Ah}{k_B T} \right)$$

$$\Rightarrow \Delta S^\ddagger = (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \left(\frac{(2.5 \times 10^{16} \text{ s}^{-1})(6.626 \times 10^{-34} \text{ Js})}{e(1.38 \times 10^{-23} \text{ JK}^{-1})(300\text{K})} \right)$$

$$\Rightarrow \Delta S^\ddagger = 60.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

$$\Rightarrow \Delta G^\ddagger = 269505 \text{ J mol}^{-1} - (300\text{K}) \times (60.6 \text{ J K}^{-1} \text{ mol}^{-1})$$

$$\Rightarrow \Delta G^\ddagger = 251.3 \text{ kJ mol}^{-1}$$