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 J = 0.0821 atm dm$^3$) K$^{-1}$ mol$^{-1}$, $k_B$=1.38x10$^{-23}$ J/K, $h$=6.626 x 10$^{-34}$ Js, 1 Torr=133.3 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 $A + B \rightarrow \textit{products}$, 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 $\Delta G^0$ 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.
\[ N_2O_4(g) \leftrightarrow NO_2(g) \]  \hspace{1cm} \text{True}

13. Chemisorption generally increases with increasing temperature till a critical value. \hspace{1cm} \text{True}

14. In collision theory, the pre-exponential factor is a measure of the rate at which collisions occur in the gas. \hspace{1cm} \text{True}

15. Multilayer adsorption is generally physisorption. \hspace{1cm} \text{True}

16. For a reaction \( A + B \rightarrow \text{products} \), if \([A] \gg [B]\), the reactant with lower concentration determines the order of the reaction. \hspace{1cm} \text{True}

17. In a microcanonical ensemble the energy of the system can fluctuate. \hspace{1cm} \text{False}

18. When a system undergoes spontaneous change at constant \( T \) and \( P \), the Gibbs energy decreases until equilibrium is reached. \hspace{1cm} \text{True}

19. The rate of an enzyme catalyzed reaction will be exactly half of the maximum rate, when \([\text{substrate}] = \text{Michaelis constant} \). \hspace{1cm} \text{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. \hspace{1cm} \text{False}

Answer all the following questions.

21. The vapor pressure of benzene between 10 °C and 30 °C fits the expression
\[ \log(p/Torr) = 7.960 - \frac{1780(K)}{T} \]. Calculate the enthalpy of vaporization. \text{3 marks}

\text{Ans:}

\[ \log p = 7.960 - 1780/T \quad \text{(given)} \]  \hspace{1cm} (1)

\[ \log p = \text{constant} - \frac{\Delta_{\text{vap}}H}{2.303RT} \]  \hspace{1cm} (2)

Comparing (1) and (2)
\[ \Delta_{\text{vap}}H = 2.303 \times 1780K \times 8.314JK^{-1}mol^{-1} \]
\[ = 34.08KJmol^{-1} \]
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.

Ans:

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

\[
dG_m = -S_m dT + V_m dp
\]

\[
\left( \frac{\partial G_m}{\partial p} \right)_T = V_m
\]

\[
\left( \frac{\partial G_m}{\partial p} \right)_T = \frac{RT}{p} + B + 3Cp + 3Dp^2
\]

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

\[
V_m = \frac{RT}{p} + B + 3Cp + 3Dp^2
\]

23. The enzyme catalyzed conversion of a substrate at 25 \(^\circ\)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?

Ans:

Maximum velocity = \( k_b[E]_0 \)

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

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

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

\[
k_b[E]_0 = \left( \frac{K_M + [S]}{[S]} \right) v = \frac{0.035 + 0.110}{0.110} \times 1.15 \times 10^{-3} = 1.52 \times 10^{-3} \text{ M s}^{-1}\]
24. In the stratosphere, the key reaction for the O₃ dissociation is \( Cl + O_3 \rightarrow ClO + O_2 \)

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 \(T = 220K\)?

(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.)

Ans:

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

(a) \( Rate_{220K} = 1.7 \times 10^{10} \, \text{M}^{-1} \, \text{s}^{-1} \, e^{-\frac{260K}{220K}} \times [5 \times 10^{-17} \, \text{M}][8 \times 10^{-9} \, \text{M}] = 2.08 \times 10^{-15} \, \text{Ms}^{-1} \)

(b) \( 1.56 \times 10^{-15} \, \text{Ms}^{-1} = 1.7 \times 10^{10} \, \text{M}^{-1} \, \text{s}^{-1} \, e^{-\frac{260K}{T}} \times [3 \times 10^{-15} \, \text{M}][8 \times 10^{-11} \, \text{M}] \)

\( \Rightarrow T = 270K \)

25. For the sequential reaction \( A \rightarrow B \rightarrow C \) 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.

where, \([B] = \frac{k_1[A]_0}{k_2 - k_1} (e^{-k_1t} - e^{-k_2t})\)

Ans:

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

\[
\frac{d[B]}{dt} = 0 = \frac{k_1[A]_0}{k_2 - k_1} \left[ -k_1 e^{-k_1t} + k_2 e^{-k_2t} \right]
\]

\( \Rightarrow k_1 e^{-k_1t} = k_2 e^{-k_2t} \Rightarrow \ln \left( \frac{k_1}{k_2} \right) t_{max} \)

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

\( \Rightarrow t_{max} = \frac{1}{(5 - 3) \times 10^6 \, \text{s}^{-1}} \ln \left( \frac{5 \times 10^6 \, \text{s}^{-1}}{3 \times 10^6 \, \text{s}^{-1}} \right) = 2.55 \times 10^{-7} \, \text{s} \)
26. Calculate the number of oxygen molecules striking 1 cm$^2$ of a surface in 1 sec 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/cm$^2$ and assuming that every oxygen molecule that strikes sticks, calculate the fraction of the surface covered.

Ans:

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

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

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

Therefore, the fraction of surface covered $= \frac{3.60 \times 10^{14}}{10^{15}} = 0.36$ (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.

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

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

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 mechanism is suggested: $A \rightarrow A^* \quad A^* + A \rightarrow A_2$

where $k_2 >> k_1$. (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 $[A] = 0.0125$ M? 

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

\[
\begin{align*}
2A & \rightarrow A_2 \\
\frac{[A]}{[A]} & = k_1 [A] - k_2 [A^*][A] \\
k_2 [A^*] & = k_1 \\
[A^*] & = \frac{k_1}{k_2} \\
rate & = \frac{1}{2} \frac{d[A]}{dt} = k_2 [A^*][A] = k_1 [A] \\
rate & = 2k_1 [A] = k [A] \quad (\Rightarrow k_1 = \frac{k}{2})
\end{align*}
\]

(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,

\[ CH_3NC \rightarrow CH_3CN \]

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 \( \Delta H^\# \) and \( \Delta S^\# \) for this reaction with \( T = 300K \). 6 marks

Ans:

This is a unimolecular reaction.

\[ \Delta H^\# = E_a - RT = 272000 \text{ J mol}^{-1} - (8.314 J K^{-1} \text{ mol}^{-1})(300K) \]
\[ \Rightarrow \Delta H^\# = 269505 \text{ J mol}^{-1} = 269.5 \text{ kJ mol}^{-1} \]

\[ \Delta S^\# = R \ln \left( \frac{A}{k_BT} \right) \]
\[ \Rightarrow \Delta S^\# = (8.314 J K^{-1} \text{ mol}^{-1}) \ln \left( \frac{(2.5 \times 10^{16} \text{ s}^{-1})(6.626 \times 10^{-34} \text{ Js})}{e(1.38 \times 10^{-23} J K^{-1})(300K)} \right) \]
\[ \Rightarrow \Delta S^\# = 60.6 J K^{-1} \text{ mol}^{-1} \]

\[ \Delta G^\# = \Delta H^\# - T \Delta S^\# \]
\[ \Rightarrow \Delta G^\# = 269505 \text{ J mol}^{-1} - (300K) \times (60.6 J K^{-1} \text{ mol}^{-1}) \]
\[ \Rightarrow \Delta G^\# = 251.3 \text{ kJ mol}^{-1} \]