Equilibrium & Reaction Rate

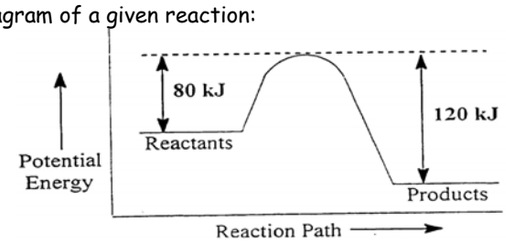
1. One of the important reactions in coal gasification is the catalytic methanation reaction:

$$CO(g) + 3H_2(g) \leftrightarrows H_2O(g) + CH_4(g) \qquad \Delta H^\circ = -206 \text{ kJ}$$

   a) Predict the direction in which this equilibrium shifts in response to an increase in temperature, and give the reason. (Value: 2)

   b) Predict the direction in which this equilibrium shifts in response to an increase in pressure caused by a decrease in reaction volume, and give the reason. (Value: 2)

2. This is the potential energy diagram of a given reaction:



   a) What is the activation energy of the forward reaction? (Value: 1)

   b) What is the ΔH of the forward reaction? (Value: 1)

   c) Sketch, on the diagram, a possible energy curve if the same reaction were to be catalyzed. (Value: 1)

   d) Explain, with reference to the diagram, how a catalyst affects the rates of both the forward and reverse reactions. (Value: 1)

3. The activation energy for the process below is 155 kJ. $H_2 + Cl_2 \leftrightarrows 2HCl + 184$ kJ

   a) Draw a potential energy diagram for this reaction. Label the axes. Label the parts of the diagram that represent the reactants, the products, the activated complex, the activation energy for the forward reaction, and the ΔH. (Value: 3)

   b) What is the activation energy for the decomposition of HCl to give H_2 and Cl_2? (Value: 1)

4. Consider the equation: $Br_2(g) \leftrightarrows 2Br(g)$ $K = 1.04 \times 10^{-3}$ at a constant temperature
   If a 0.200 L vessel contains 4.34×10^{-2} mol of Br_2 at equilibrium, what concentration of Br is present? (Value: 4)

5. Consider the following reaction: $3\,X(g) + Y(g) \leftrightarrows 2\,W(g) + Z(g)$
   At 298 K the equilibrium concentrations of X, Y, W, and Z were found to be 7.0 mol/L, 6.0 mol/L, 5.0 mol/L, and 7.0 mol/L, respectively. When the temperature was raised to 313 K the new equilibrium concentration of Z was found to be 6.0 mol/L.

   a) What are the new equilibrium concentrations of the other three substances? (Value: 3)

   b) What is the new K_{eq}? (Value: 1)

6. Draw a potential energy diagram for a reaction in which the heat of reaction is $\Delta H = -80$ kJ/mol; and the activation energy is 28 kJ/mol. Label both axes, the activation energy, heat of reaction, site of activated complex, reactants and products. Show on the diagram, using a dashed line, how a catalyst is effective in increasing the reaction rate. (Value: 3)

7. The activation energy for the decomposition of hydrogen peroxide, H_2O_2, is estimated to be 75 kJ/mol, while the activation energy for the reaction catalyzed by I^- is 48 kJ/mol. The mechanism of the catalyzed reaction is thought to be:

$$H_2O_2(aq) + I^-(aq) \rightarrow H_2O(l) + IO^-(aq) \qquad \text{(slow)}$$
$$IO^-(aq) + H_2O_2(aq) \rightarrow H_2O(l) + O_2(g) + I^-(aq) \qquad \text{(fast)}$$

   a) What is a reactive intermediate in this mechanism? (Value: 1)

   b) Explain why $I^-(aq)$ is a catalyst. (Value: 1)

   c) Write the balanced equation for the overall reaction. (value: 1)

   d) Sketch an unlabelled energy profile curve for the uncatalyzed exothermic reaction. (Value: 1)

8. Explain the effect a catalyst has on a system that is already at equilibrium. (Value: 2)

9. The Deacon process is used to make chlorine gas from hydrogen chloride, especially in situations where a large amount of by-product HCl is available from other chemical processes.

$$4\,HCl(g) + O_2(g) \leftrightarrows 2\,H_2O(g) + 2\,Cl_2(g) \qquad \Delta H = -114 \text{ kJ}$$

   A mixture of HCl, O_2, H_2O, and Cl_2 is brought to equilibrium in a 2.00 L closed flask at 400°C. What will be the effect on the equilibrium amount of $Cl_2(g)$ if:

   a) additional $O_2(g)$ is added to the mixture at constant volume? (Value: 1)

   b) HCl(g) is removed from the reaction mixture at constant volume. (Value: 1)

   c) the mixture is transferred to a vessel of twice the volume as the original equilibrium volume? (Value: 1)

   d) the temperature is raised to 500°C? (Value: 1)

   e) When 2.50 mol of HCl(g), and 1.60 mol of $O_2(g)$ are mixed in the flask and allowed to come to equilibrium, 0.60 mol of $Cl_2(g)$ were obtained. Calculate the equilibrium constant, Keq, for this reaction. (Value: 3)

   f) At these conditions, are the reactants or products favoured? Explain briefly. (Value: 1)

10. Ammonia is manufactured by the reaction between nitrogen and hydrogen, using the Haber process:

$$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$$

   a) State and explain the effect of increasing the concentrations of the reactants on the yield of ammonia obtained. (Value: 2)

   b) State and explain the effect of using a catalyst on the yield of ammonia obtained. (Value: 2)

11. When 0.100 mol of $N_2(g)$ and 0.300 mol of $H_2(g)$ are placed in a 1.00 L container, some $NH_3(g)$ forms before equilibrium is reached. $N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$ Only 0.022 mol of $N_2(g)$ reacted, and 0.078 mol remains unreacted.
    a) What is the equilibrium concentration of each substance? (Value: 2)
    b) Calculate the numerical value for the equilibrium constant for this system. (Value: 2)

12. Consider the five reactions whose activation energies (E_a) and ΔH values are listed in the table.

Reaction	E_a (kJ/mol)	ΔH (kJ/mol)
A	60	20
B	6	3
C	50	30
D	5	-1000
E	100	-30

    a) Which one of the reactions represents:
        i) the slowest reaction. (Value: 1)
        ii) an explosive exothermic reaction. (Value: 1)
        iii) a spontaneous endothermic reaction. (Value: 1)
    b) If a catalyst were added to reaction A, what would be the effect on the values of E_a and ΔH given in the table for that reaction? (Value: 1)

13. At 1495°C the equilibrium, $H_2(g) + Br_2(g) \leftrightarrows 2HBr(g)$, has an equilibrium constant that equals 3.5×10^4. If the equilibrium concentrations of H_2 and Br_2 are 0.010 mol/L and 0.020 mol/L respectively, what is the equilibrium concentration of HBr? (Value: 2)

14. At 21.8°C the equilibrium, $NH_4HS(s) \leftrightarrows NH_3(g) + H_2S(g)$, has an equilibrium constant that equals 1.2×10^{-4}. A sample of solid NH_4HS is placed in a closed container and allowed to decompose until equilibrium is reached at 21.8°C. Calculate the equilibrium concentrations of NH_3 and H_2S. (Value: 2)

15. Consider the reaction: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$
    yellow colourless colourless colourless
    a) Suggest a method for measuring the rate of this reaction. (Value: 1)
    b) Define the rate of this reaction qualitatively. (Value: 1)

16. Distinguish an activated complex from a catalyst by stating:
    a) how they are different. (Value: 2)
    b) how they are alike. (Value: 2)

17. The air we breathe is composed of $N_2(g)$ and $O_2(g)$. A reaction between these two elements to form NO(g) occurs under the appropriate conditions. At 37°C, the equilibrium constant for this reaction is 1×10^{-12}.
    $N_2(g) + O_2(g) \leftrightarrows 2NO(g)$
    a) Write the equilibrium constant expression for this reaction. (Value: 1)
    b) Which will have the higher concentration: $N_2(g)$ and $O_2(g)$ or NO(g) at equilibrium at 37°C? Justify your answer. (Value: 2)
    c) What will happen to the amount of $N_2(g)$ if the concentration of $O_2(g)$ is decreased? (Value: 1)

18. Consider the equilibrium: $Br_2(g) \leftrightarrows 2Br(g)$ $K = 1.26 \times 10^{-3}$ at a constant temperature
    If a 0.200 L vessel contains 3.44×10^{-2} mol of Br_2 at equilibrium, what concentration of Br is present? (Value: 4)

19. An equilibrium mixture of SO_2, O_2, and SO_3 contains equal concentrations (1.0 mol/L) of SO_2 and SO_3:
    $2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g)$ $K = 2.7 \times 10^2$ Calculate the equilibrium concentration of O_2. (Value: 2)

20. Chlorine and iodine react to form ICl: $I_2(g) + Cl_2(g) \leftrightarrows 2ICl(g)$ $K = 9.1$
    A 1.00 L reaction vessel contains a mixture of 0.0091 mol ICl and 0.0050 mol each of I_2 and Cl_2. Is the reaction at equilibrium or does it move in the forward or reverse direction? Show the calculations that enable you to answer this question. (Value: 4)

21. Sketch a potential energy diagram for the reaction of nitrogen dioxide with oxygen:
    $NO_2(g) + O_2(g) \leftrightarrows NO(g) + O_3(g)$ $\Delta H = +199$ kJ
    The value of the activation energy (Ea) for the forward reaction is 209 kJ/mol. Your sketch should show the values of the forward and reverse activation energies and ΔH. (Value: 4)

22. An experiment starting with no NO_2 and a concentration of N_2O_4 equalling 0.0200 mol/L was allowed to reach equilibrium: $N_2O_4(g) \leftrightarrows 2NO_2(g)$
    The equilibrium concentration of N2O4 was 0.0045 mol/L .
    a) What was the equilibrium concentration of NO_2? (Value: 2)
    b) What is the numerical value of the equilibrium constant for the equilibrium? (Value: 2)

23. When win spoils, C_2H_5OH is changed to CH_3COOH as oxygen from the air reacts with it:
    $C_2H_5OH(aq) + O_2(g) \leftrightarrows CH_3COOH(aq) + H_2O(l)$ $K = 1.2 \times 10^{82}$
    Will much C_2H_5OH remain when the reaction reaches equilibrium? Explain your answer? (Value: 2)

24. The decomposition of HI(g) to $H_2(g)$ and $I_2(g)$ was followed by measuring the concentration of iodine colorimetrically:

Time (h)	$[I_2]$
0.0	0.0
0.5	2.2×10^{-4}
2.0	3.9×10^{-4}
4.0	4.9×10^{-4}
7.0	5.6×10^{-4}
10.0	5.8×10^{-4}
12.0	5.8×10^{-4}
14.0	5.8×10^{-4}

    a) Graph $[I_2]$ versus time. (Value: 1)
    b) Show the effect of a catalyst with a broken line on your graph. (Value: 1)
    c) If the equilibrium constant for the reaction, $2HI(g) \leftrightarrows H_2(g) + I_2(g)$, equals 1.83×10^{-2}, determine the equilibrium concentration of HI. (Value: 2)