Midterm 2

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1. A system contains three molecular species A, B and C that react according to the reaction A + 2B $\rightleftarrows$ C. When the system reaches equilibrium at standard conditions, the concentrations are found to be: [A] = 5.7×10^{-2} mol/l, [B] = 3.2×10^{-2} mol/l, [C] = 9.7×10^{-2} mol/l.

(a) Determine the standard free energy change for this reaction $\Delta G°$.

(b) For the reaction F $\rightleftarrows$ 2C, the standard free energy change for the reaction $\Delta G°$ is 40.2 kJ/mol. If the two coupled reactions

$$A + 2B \rightleftarrows C \qquad \text{(i)}$$
$$2C \rightleftarrows F \qquad \text{(ii)}$$

occur at standard conditions, when the system reaches equilibrium, will [F]/[A] be large or small? Justify your answer quantitatively.

(c) Initially the system undergoing the coupled reactions in part (b) contains only species A and B and a catalyst that reduces the activation energy for reaction (i) by 25.2 kJ/mol. Will this change the [F]/[A] ratio at equilibrium? Explain your answer.

(d) For the reaction F $\rightleftarrows$ 2C described in part (b), what are the units on the equilibrium constant?

(a) $$K_{eq} = \frac{[C]_e}{[A]_e[B]_e^2} = \frac{9.7\times10^{-2}}{(5.7\times10^{-2})(3.2\times10^{-2})^2} = 1662$$

$$\Delta G^\circ = -\bar{R}T \ln K_{eq} = -(8.315)(298)\ln(1662) = -18380 \text{ J/mol} = -18.4 \text{ kJ/mol}$$

(b) $A + 2B \rightleftarrows C \quad \Delta G^\circ = -18.4$ kJ/mol

$C \rightleftarrows \frac{1}{2}F \quad \Delta G^\circ = -40.2/2$

$$\Delta G^\circ_{\text{coupled}} = -18.4 - 20.1 = -38.5 \text{ kJ/mol}$$

since $\Delta G^\circ_{\text{coupled}} < 0 \Rightarrow$ system will drive reaction forward

$\Rightarrow$ [F]/[A] will be large.

(c) The catalyst affects only the rate, not the equilibrium concentrations

(d) $$K_{eq} = \frac{[C]^2}{[F]} \sim \frac{[\text{mol}/l]^2}{\text{mol}/l} \sim \text{mol}/l.$$

2. Consider the chemical reaction

$$2A \rightleftarrows 2B + C$$

The standard free energy change for this reaction is $\Delta G^{\circ\prime} = -20.5$ kJ/mol. Below is a table of measured reaction rates at different temperatures and concentrations of A.

T (°C)	[A] (mol/l)	(1/2)d[A]/dt ((mol/l)/s)
25	0.01	0.0024
25	0.02	0.0096
31	0.01	0.0033

(a) Assuming that the Arrhenius model for the rate constant applies, write down the appropriate relation for the reaction rate $J = -(\frac{1}{2})d[A]/dt$ as a function of activation free energy ΔG_a, temperature and species concentration. You may assume that the order of the equation is indicated by the stoichiometric coefficients.

(b)Use the measured data in the table above to determine the activation free energy for this reaction.

(c) Draw the free energy vs. reaction coordinate diagram for this reaction and indicate the changes in free energy associated with formation of the transition state and the products.

(a) $J = -(\frac{1}{2})\frac{d[A]}{dt} = k' e^{-\Delta G_a/\bar{R}T}[A]^2$

$\ln J = \ln k' - \Delta G_a/\bar{R}T + 2\ln[A]$

$\ln J_1 = \ln k' - \Delta G_a/\bar{R}T_1 + 2\ln[A]_1$

$\ln J_3 = \ln k' - \Delta G_a/\bar{R}T_3 - 2\ln[A]_3$

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$\ln(J_1/J_3) = \frac{\Delta G_a}{\bar{R}}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) + 2\ln([A]_1/[A]_3)$ ← solve for ΔG_a.

$$\Delta G_a = \frac{8.315\ln(.0024/.0033)}{\left(\frac{1}{304} - \frac{1}{298}\right)} = \boxed{39980\ \frac{J}{mol} = \underline{\underline{39.98}}\ \frac{kJ}{mol}}$$