Temperature Dependence of the Equilibrium Constant

Name

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1. For the reaction

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

the following data was collected for the magnitude of the equilibrium constant at different temperatures. Complete the columns 1/T (K) and ln (K).

Temperature (K)	1/T (K)	К	ln (K)
273	0.003663	72.9	4.289
280	0.003571	38.8	3.658
290	0.003448	16.6	2.809
298	0.003356	8.8	2.175
305	0.003279	5.2	1.649
315	0.003175	2.5	0.916
325	0.003077	1.3	0.262

The graph of this data



a. How does the equilibrium constant change with temperature?

The equilibrium constant decreases as the temperature increases.

b. Is the reaction exothermic or endothermic?

Increasing the temperature of the reaction container is the same as adding heat to the reaction system. Since the equilibrium constant is decreasing as heat is added, this means the amounts of products are decreasing and the amount of reactants are increasing. So the reaction is shifting from right to left. For this to happen 'heat' must be on the products side of the reaction, therefore the reaction is exothermic. This makes sense because the reaction is forming a N-N bond, forming bonds is an exothermic process.

c. What does a plot of ln (K) (y-axis) versus 1/T (Kelvin) (x-axis) look like?



d. If the slope of the line in the plot is equal to $-\Delta H^{\circ}/R$ (where R is 8.314 J mol⁻¹ K⁻¹), what is ΔH° for the reaction?

From the graph the slope is 6881 K⁻¹.

 $6881 \text{ K}^{-1} = -\frac{\Delta \text{H}^{\circ}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}$ $\Delta \text{H}^{\circ} = -6881 \text{ K}^{-1} \cdot 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ $\Delta \text{H}^{\circ} = -57,208 \text{ J mol}^{-1} = -57.2 \text{ kJ mol}^{-1}$

e. Estimate the value of K at 278 K.

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The equation of the line from the graph is y = 6881 x - 20.916

If we rewrite the equation with the axis functions, the equation is $\ln (K) = 6881 \ 1/T - 20.916$

If
$$I = 2/8$$
 K
ln (K) = 6881 · 1/278 - 20.916 = 3.836
 $e^{\ln K} = e^{3.836}$
K = 46.3

f.Estimate the temperature (Kelvin) when the equilibrium constant is 100

The equation of the line from the graph is y = 6881 x - 20.916

If we rewrite the equation with the axis functions, the equation is $\ln (K) = 6881 \ 1/T - 20.916$

If K = 100

 $ln (100) = 6881 \cdot 1/T - 20.916 = 3.836$ 4.5605 = 6881 \cdot 1/T - 20.916 T = 6881/(20.916 + 4.5605) = 270

2. In the reaction

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

 $\Delta H = -57.2 \text{ kJ mol}^{-1}$ at 25 °C. The equilibrium constant, K_p, at this temperature is 8.8. Calculate K_p at 0 °C.

$$\ln \frac{K_{1}}{K_{2}} = \frac{\Delta H_{rxn}}{R} \left(\frac{1}{T_{2}} \cdot \frac{1}{T_{1}} \right)$$
$$\ln \frac{K_{1}}{8.8} = \frac{-57200 \text{ J}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{298 \text{ K}} \cdot \frac{1}{273 \text{ K}} \right)$$
$$\ln \frac{K_{1}}{8.8} = 2.11$$
$$e \left(\ln \frac{K_{1}}{8.8} \right) = e^{2.11}$$
$$\frac{K_{1}}{8.8} = 8.28$$
$$K_{1} = 72.9$$

3. In the reaction

$$2ICl(g) \rightleftharpoons I_2(g) + Cl_2(g)$$

 $\Delta H = 26.9 \text{ kJ mol}^{-1}$ at 25 °C. The equilibrium constant, K_c, at this temperature is 4.9 x 10⁻⁶. Calculate K_c at 100 °C.

$$\ln \frac{K_1}{K_2} = \frac{\Delta H_{rxn}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{K_1}{4.9 \text{ x } 10^{-6}} = \frac{26900 \text{ J}}{8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}} \left(\frac{1}{298 \text{ K}} - \frac{1}{373 \text{ K}}\right)$$
$$\ln \frac{K_1}{4.9 \text{ x } 10^{-6}} = 2.18$$
$$e \left(\ln \frac{K_1}{4.9 \text{ x } 10^{-6}} \right) = e^{2.18}$$
$$\frac{K_1}{4.9 \text{ x } 10^{-6}} = 8.87$$
$$K_1 = 4.3 \text{ x } 10^{-5}$$

1a. Write the general mathematical equation which relates the equilibrium constant for a chemical reaction to temperature.

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_{rxn}}{R} \left(\frac{1}{T_2} \cdot \frac{1}{T_1} \right)$$

b. Define each of the variables in this equation.

 K_1 and K_2 are both equilibrium constants at T_1 and T_2 , respectively. ΔH_{rxn} is the enthalpy of reaction for the reaction and R is the ideal gas constant. The value of R is 8.314 $\frac{J}{mol \cdot K}$.