## Temperature Dependence of the Equilibrium Constant

Name
Sec

1. For the reaction

$$
2 \mathrm{NO}_{2(g)} \rightleftharpoons \mathrm{N}_{2} \mathrm{O}_{4(g)}
$$

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) | $\mathbf{1} / \mathbf{T}(\mathbf{K})$ | K | $\ln (\mathbf{K})$ |
| :---: | :---: | :---: | :---: |
| 273 | $\mathbf{0 . 0 0 3 6 6 3}$ | 72.9 | $\mathbf{4 . 2 8 9}$ |
| 280 | $\mathbf{0 . 0 0 3 5 7 1}$ | 38.8 | $\mathbf{3 . 6 5 8}$ |
| 290 | $\mathbf{0 . 0 0 3 4 4 8}$ | 16.6 | $\mathbf{2 . 8 0 9}$ |
| 298 | $\mathbf{0 . 0 0 3 3 5 6}$ | 8.8 | $\mathbf{2 . 1 7 5}$ |
| 305 | $\mathbf{0 . 0 0 3 2 7 9}$ | 5.2 | $\mathbf{1 . 6 4 9}$ |
| 315 | $\mathbf{0 . 0 0 3 1 7 5}$ | 2.5 | $\mathbf{0 . 9 1 6}$ |
| 325 | $\mathbf{0 . 0 0 3 0 7 7}$ | 1.3 | $\mathbf{0 . 2 6 2}$ |

The graph of this data

## Q1 Data Plot


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 $\mathrm{N}-\mathrm{N}$ bond, forming bonds is an exothermic process.
c. What does a plot of $\ln (\mathrm{K})(y$-axis) versus $1 / \mathrm{T}(\mathrm{Kelvin})(x$-axis) look like?

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

From the graph the slope is $6881 \mathrm{~K}^{-1}$.

$$
\begin{aligned}
& 6881 \mathrm{~K}^{-1}=-\frac{\Delta H^{\circ}}{8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}} \\
& \Delta H^{\circ}=-6881 \mathrm{~K}^{-1} \cdot 8.314 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1} \\
& \Delta H^{\circ}=-57,208 \mathrm{~J} \mathrm{~mol}^{-1}=-57.2 \mathrm{~kJ} \mathrm{~mol}^{-1}
\end{aligned}
$$

e. Estimate the value of K at 278 K .

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 $\ln (K)=68811 / T-20.916$

If $\mathbf{T}=\mathbf{2 7 8} \mathrm{K}$
$\ln (K)=\mathbf{6 8 8 1} \cdot \mathbf{1} / \mathbf{2 7 8}-\mathbf{2 0 . 9 1 6}=\mathbf{3 . 8 3 6}$
$\mathrm{e}^{\ln \mathrm{K}}=\mathrm{e}^{\mathbf{3 . 8 3 6}}$
$K=46.3$
f.Estimate the temperature (Kelvin) when the equilibrium constant is 100

The equation of the line from the graph is $y=6881 \boldsymbol{x} \mathbf{- 2 0 . 9 1 6}$

If we rewrite the equation with the axis functions, the equation is $\ln (K)=68811 / T-20.916$

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

$$
2 \mathrm{NO}_{2}(g) \rightleftharpoons \mathrm{N}_{2} \mathrm{O}_{4}(g)
$$

$\Delta \mathrm{H}=-57.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$ at $25^{\circ} \mathrm{C}$. The equilibrium constant, $\mathrm{K}_{\mathrm{p}}$, at this temperature is 8.8. Calculate $\mathrm{K}_{\mathrm{p}}$ at $0^{\circ} \mathrm{C}$.
$\ln \frac{\mathrm{K}_{1}}{\mathrm{~K}_{2}}=\frac{\Delta \mathrm{H}_{\mathrm{rxn}}}{\mathrm{R}}\left(\frac{1}{\mathrm{~T}_{2}}-\frac{1}{\mathrm{~T}_{1}}\right)$
$\ln \frac{\mathrm{K}_{1}}{8.8}=\frac{-57200 \mathrm{~J}}{8.314 \frac{\mathrm{~J}}{\mathrm{~mol} \cdot \mathrm{~K}}}\left(\frac{1}{298 \mathrm{~K}}-\frac{1}{273 \mathrm{~K}}\right)$
$\ln \frac{K_{1}}{\mathbf{8 . 8}}=\mathbf{2 . 1 1}$
$\mathrm{e}\left(\ln \frac{\mathrm{K}_{1}}{8.8}\right)=\mathrm{e}^{2.11}$
$\frac{K_{1}}{8.8}=8.28$
$K_{1}=72.9$
3. In the reaction

$$
2 \mathrm{ICl}(g) \rightleftharpoons \mathrm{I}_{2}(g)+\mathrm{Cl}_{2}(g)
$$

$\Delta \mathrm{H}=26.9 \mathrm{~kJ} \mathrm{~mol}^{-1}$ at $25^{\circ} \mathrm{C}$. The equilibrium constant, $\mathrm{K}_{\mathrm{c}}$, at this temperature is $4.9 \times 10^{-6}$. Calculate $\mathrm{K}_{\mathrm{c}}$ at $100^{\circ} \mathrm{C}$.
$\ln \frac{K_{1}}{K_{2}}=\frac{\Delta H_{r x n}}{R}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)$

$$
\ln \frac{\mathrm{K}_{1}}{4.9 \times 10^{-6}}=\frac{26900 \mathrm{~J}}{8.314 \frac{\mathrm{~J}}{\mathrm{~mol} \cdot \mathrm{~K}}}\left(\frac{1}{298 \mathrm{~K}}-\frac{1}{373 \mathrm{~K}}\right)
$$

$$
\ln \frac{K_{1}}{4.9 \times 10^{-6}}=2.18
$$

$$
\mathrm{e}\left(\ln \frac{\mathrm{~K}_{1}}{4.9 \times 10^{-6}}\right)=\mathrm{e}^{2.18}
$$

$$
\frac{K_{1}}{4.9 \times 10^{-6}}=8.87
$$

$$
K_{1}=4.3 \times 10^{-5}
$$

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

$$
\ln \frac{K_{2}}{K_{1}}=-\frac{\Delta H_{\mathrm{rxn}}}{\mathrm{R}}\left(\frac{1}{T_{2}}-\frac{1}{T_{1}}\right)
$$

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. $\Delta H_{r x n}$ is the enthalpy of reaction for the reaction and $R$ is the ideal gas constant. The value of $R$ is $8.314 \frac{\mathrm{~J}}{\mathrm{~mol} \cdot \mathrm{~K}}$.

