

02/20/02

- Exam Solution Key now online 😊
- Exams not graded yet ☹
- Chapter 12 problems now assigned ☹
- Chapter 12 solutions now online 😊

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What is K at 1000 K?

Here's what we know:

$$\begin{array}{ll} K_1 = 7.71 \times 10^2 & K_2 = ? \\ T_1 = 298.15 \text{ K} & T_2 = 1000. \text{ K} \end{array}$$

Invoking van't Hoff:

$$\ln(K_2/K_1) = -(\Delta H^\circ/R)(1/T_2 - 1/T_1)$$

$$\ln(K_2/K_1) = -(-46,110 \text{ J}/8.3145 \text{ J/mol}\cdot\text{K})[1/1000 - 1/298.15]$$

$$\ln(K_2/K_1) = (5.5457 \times 10^3)[-2.354 \times 10^{-3}] = \mathbf{-13.0547}$$

$$K_2/K_1 = e^{-13.0547} = 2.1399 \times 10^{-6}$$

$$K_2 = (2.1399 \times 10^{-6})(7.71 \times 10^2) = 1.6502 \times 10^{-3} = \mathbf{\underline{\underline{1.7 \times 10^{-3}}}}$$

Equilibrium

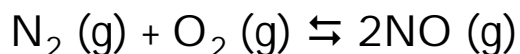
Chem 36
Spring 2002

The Equilibrium Condition

- **Recall:** a system is at *equilibrium* when $\Delta G = 0$
 - No *net* driving force for process in *either direction*
- **Equilibrium is a *dynamic* condition**
 - Reaction has not *stopped*
 - No *net change* in the amounts of products or reactants

K and *Equilibrium Position*

Case 1: K very small ($K \ll 1$)



$$K = \frac{(\text{P}_{\text{NO}})^2}{(\text{P}_{\text{N}_2})(\text{P}_{\text{O}_2})} = 1. \times 10^{-30} \quad \text{at } 25 \text{ }^\circ\text{C}$$

At equilibrium, do reactants or products predominate?

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Calculate it!

Suppose we know that:

$$\text{P}_{\text{N}_2} = \text{P}_{\text{O}_2} = 1.0 \text{ atm} \quad (\text{at equilibrium})$$

Calculate P_{NO}

Solve equilibrium constant expression for P_{NO} :

$$(\text{P}_{\text{NO}})^2 = K \text{P}_{\text{N}_2} \text{P}_{\text{O}_2} = (1. \times 10^{-30})(1.0)(1.0)$$

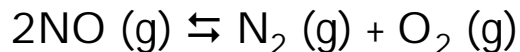
$$(\text{P}_{\text{NO}})^2 = 1. \times 10^{-30}$$

$$\text{P}_{\text{NO}} = (1. \times 10^{-30})^{1/2} = \underline{1. \times 10^{-15} \text{ atm}}$$

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Reverse it!

Case 2: K very large ($K \gg 1$)



$$K = \frac{(P_{\text{N}_2})(P_{\text{O}_2})}{(P_{\text{NO}})^2} = 1. \times 10^{30} \text{ at } 25 \text{ }^\circ\text{C}$$

At equilibrium, *products* predominate

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A Third Case

Case 3: $K \approx 1$



$$K = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = 11. \text{ At } 100 \text{ }^\circ\text{C}$$

Here, we expect to have *similar* amounts of products and reactants

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Calculate!

Suppose we know that:

$$P_{\text{N}_2\text{O}_4} = 1.0 \text{ atm (at equilibrium)}$$

Calculate P_{NO_2}

Solve equilibrium constant expression for P_{NO_2} :

$$(P_{\text{NO}_2})^2 = K P_{\text{N}_2\text{O}_4} = (11.)(1.0)$$

$$(P_{\text{NO}_2})^2 = 11.$$

$$P_{\text{NO}_2} = (11.)^{1/2} = \underline{\underline{3.3 \text{ atm}}}$$

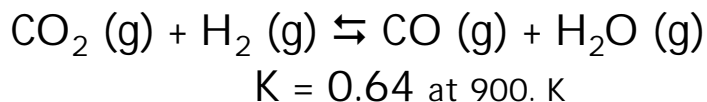
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Are we there yet?

- How do we know whether a system is at equilibrium?
 - **Evaluate ΔG** (*lotsa work!*): $\Delta G = \Delta G^\circ + RT \ln Q$
 - **Calculate Q** and compare with K
 1. If $Q < K$: ΔG is *negative* (rxn proceeds forward)
 2. If $Q > K$: ΔG is **positive** (rxn proceeds in reverse)
 3. If $Q = K$: $\Delta G = 0$ (system is AT equilibrium)

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Example



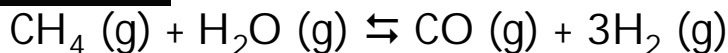
• If we have **1 atm of each gas**, in which direction will reaction proceed spontaneously?

$$Q = \frac{P_{\text{CO}} P_{\text{H}_2\text{O}}}{P_{\text{CO}_2} P_{\text{H}_2}} = \frac{(1)(1)}{(1)(1)} = 1 > 0.64 = K$$

$Q > K$: Reverse Rxn is Spontaneous

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Example: Calculating K



At equilibrium (at 600 K):

P, atm: 1.40 2.30 1.60 7.1 x 10⁻³

Into the equilibrium constant expression:

$$K = \frac{(P_{\text{CO}})(P_{\text{H}_2})^3}{(P_{\text{CH}_4})(P_{\text{H}_2\text{O}})} = \frac{(1.60)(7.1 \times 10^{-3})^3}{(1.40)(2.30)}$$

Not always quite so easy!

$$K = 1.8 \times 10^{-7}$$

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