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:

$K_1 = 7.71 \times 10^2$ $K_2 = ?$

$T_1 = 298.15$ K $T_2 = 1000.$ K

Invoking van't Hoff:

$$\mathbf{Ln(K_2/K_1) = -(\Delta H^o/R)(1/T_2 - 1/T_1)}$$

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

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

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

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

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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

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K and *Equilibrium Position*

Case 1: K *very* small (K << 1)

N_2 (g) + O_2 (g) ⇆ 2NO (g)

$$K = \frac{(P_{NO})^2}{(P_{N2})(P_{O2})} = 1.\ X\ 10^{-30} \quad \text{at } 25\ ^oC$$

At equilibrium, do reactants or products predominate?

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Calculate it!

Suppose we know that:

$P_{N2} = P_{O2} = 1.0$ atm (at equilibrium)

Calculate P_{NO}

Solve equilibrium constant expression for P_{NO}:

$\mathbf{(P_{NO})^2 = K\ P_{N2}P_{O2}} = (1.\ x\ 10^{-30})(1.0)(1.0)$

$\mathbf{(P_{NO})^2} = \boldsymbol{1.\ x\ 10^{-30}}$

$P_{NO} = (1.\ X\ 10^{-30})^{½} =$ ***1. x 10^{-15} atm***

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Reverse it!

Case 2: K *very* large (K >> 1)

$$2NO\ (g) \leftrightarrows N_2\ (g) + O_2\ (g)$$

$$K = \frac{(P_{N2})(P_{O2})}{(P_{NO})^2} = 1.\ X\ 10^{30} \quad \text{at } 25\ ^oC$$

At equilibrium, *products* predominate

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A Third Case

Case 3: $K \approx 1$

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

$$K = \frac{(P_{NO2})^2}{P_{N2O4}} = 11. \quad \text{At } 100\ ^oC$$

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

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Calculate!

Suppose we know that:

$P_{N2O4} = 1.0$ atm (at equilibrium)

Calculate P_{NO2}

Solve equilibrium constant expression for P_{NO2}:

$(P_{NO2})^2 = K\ P_{N2O4} = (11.)(1.0)$

$(P_{NO2})^2 = 11.$

$P_{NO2} = (11.)^{1/2} =$ ***3.3 atm***

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Are we there yet?

- How do we know whether a system is at equilibrium?
  - **Evaluate DG** (*lotsa work!*): $\Delta G = \Delta G^o + RT\ln Q$
  - **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

$CO_2\ (g) + H_2\ (g) \leftrightarrows CO\ (g) + H_2O\ (g)$

$K = 0.64$ at 900. K

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

$$Q = \frac{P_{CO}\,P_{H2O}}{P_{CO2}\,P_{H2}} = \frac{(1)(1)}{(1)(1)} = 1 > \mathit{0.64 = K}$$

Q > K: *Reverse Rxn is Spontaneous*

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Example: Calculating K

$CH_4\ (g) + H_2O\ (g) \leftrightarrows CO\ (g) + 3H_2\ (g)$

At equilibrium (at 600 K):

<u>P, atm:</u>	1.40	2.30	1.60	7.1×10^{-3}

Into the equilibrium constant expression:

$$K = \frac{(P_{CO})(P_{H2})^3}{(P_{CH4})(P_{H2O})} = \frac{(1.60)(7.1 \times 10^{-3})^3}{(1.40)(2.30)}$$

Not always quite so easy!

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

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