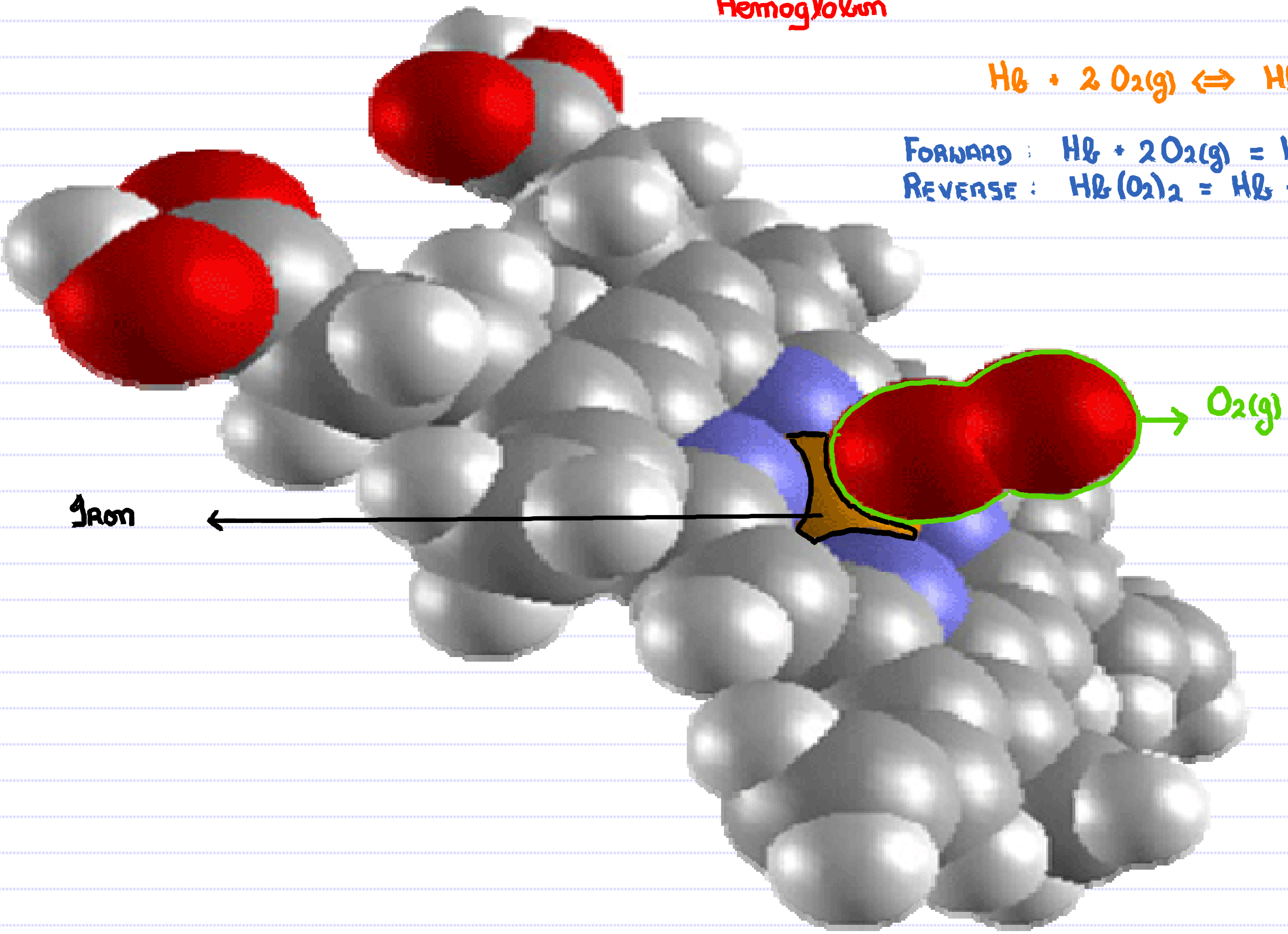
15.1 The Nature of the Equilibrium State

The Equilibrium State

Hemoglobin



$Hb + 2\,O_{2(g)} \Leftrightarrow Hb(O_2)_2$

FORWARD : $Hb + 2O_{2(g)} = Hb(O_2)_2$

REVERSE : $Hb(O_2)_2 = Hb + 2O_{2(g)}$

15.1 The Nature of the Equilibrium State

The Equilibrium State

$$Fe^{3+} + SCN^{-} \Leftrightarrow FeSCN^{2+}$$

At Equilibrium : Initial Rate of forward Reaction = Initial Rate of the Reverse Reaction.

$$k_f [Fe^{3+}][SCN^{-}] = k_R [FeSCN^{2+}]$$

$$\boxed{\frac{k_f}{k_R}} = \frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]}$$

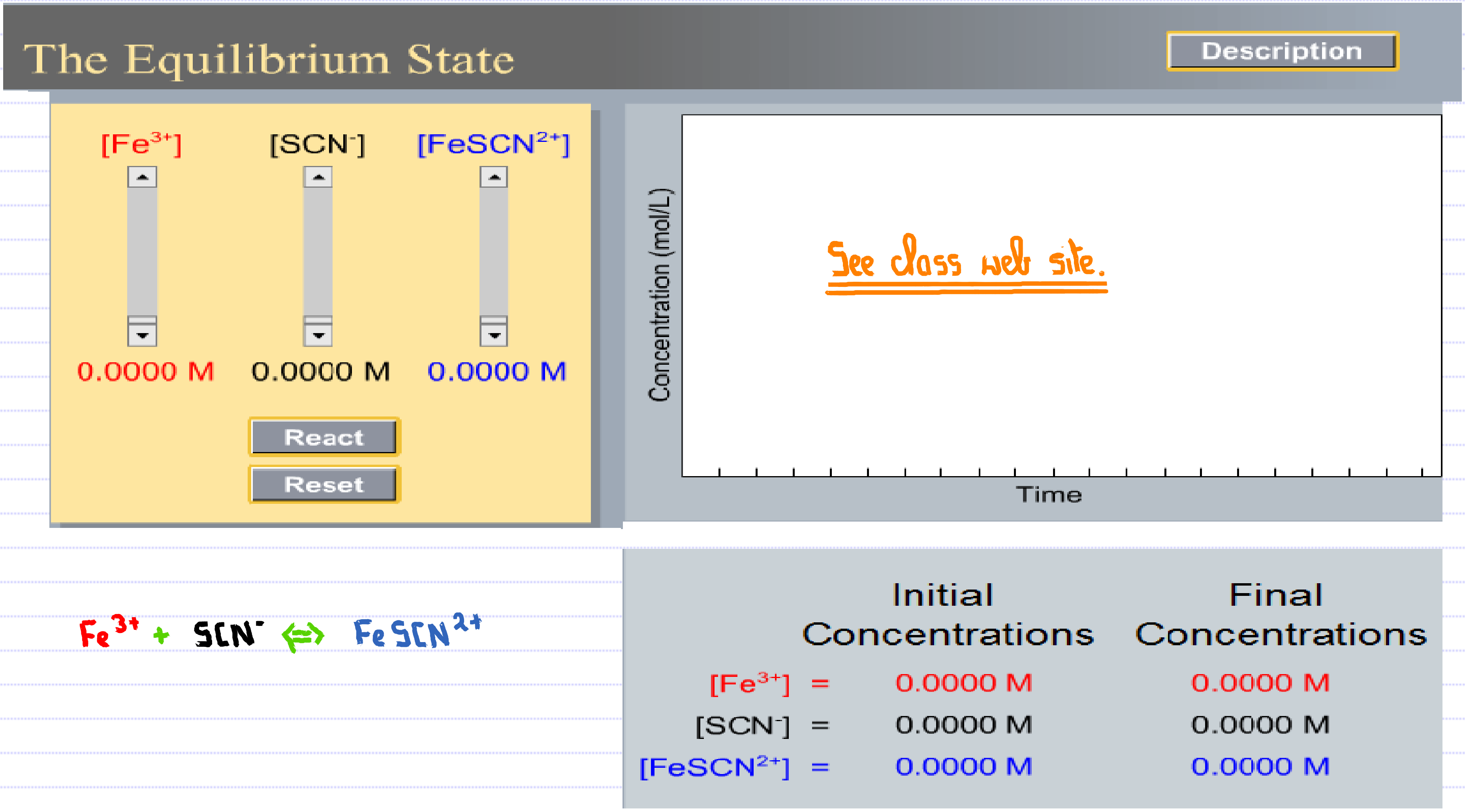
→ Constant.

$$\frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^{-}]} = \text{Constant} = K$$

? Is this true ... don't take my word for it ! ... experiment.

15.2 The Equilibrium Constant, K

The Equilibrium State



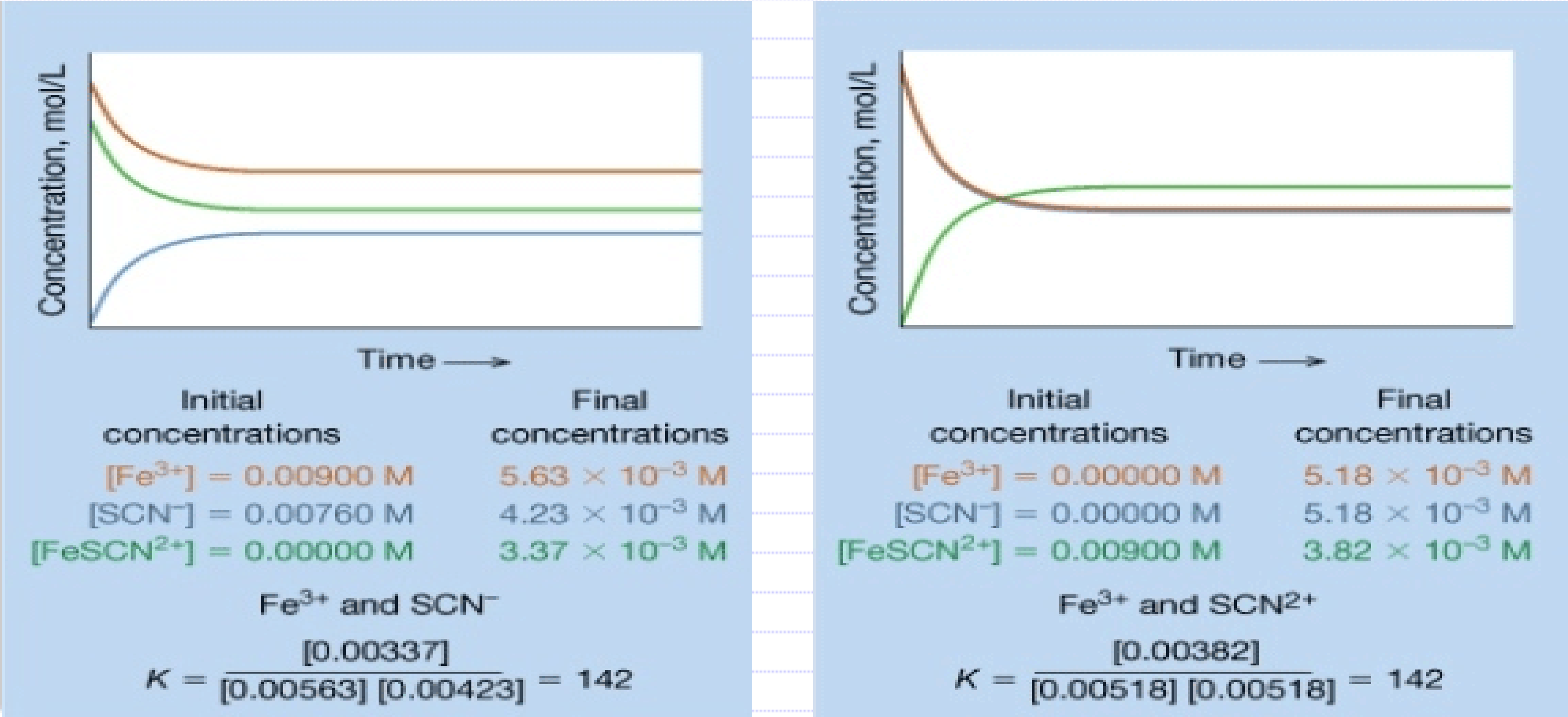
See class web site.

	Initial Concentrations	Final Concentrations
$[Fe^{3+}]$ =	0.0000 M	0.0000 M
$[SCN^-]$ =	0.0000 M	0.0000 M
$[FeSCN^{2+}]$ =	0.0000 M	0.0000 M

$Fe^{3+} + SCN^- \rightleftharpoons FeSCN^{2+}$

15.2 The Equilibrium Constant, K

Equilibrium Constants



Initial concentrations	Final concentrations
$[Fe^{3+}] = 0.00900$ M	5.63×10^{-3} M
$[SCN^-] = 0.00760$ M	4.23×10^{-3} M
$[FeSCN^{2+}] = 0.00000$ M	3.37×10^{-3} M

Fe^{3+} and SCN^-

$$K = \frac{[0.00337]}{[0.00563]\,[0.00423]} = 142$$

Initial concentrations	Final concentrations
$[Fe^{3+}] = 0.00000$ M	5.18×10^{-3} M
$[SCN^-] = 0.00000$ M	5.18×10^{-3} M
$[FeSCN^{2+}] = 0.00900$ M	3.82×10^{-3} M

Fe^{3+} and SCN^{2+}

$$K = \frac{[0.00382]}{[0.00518]\,[0.00518]} = 142$$

In general : $aA + bB \Leftrightarrow cC + dD$

$$K = \frac{[\text{PRODUCTS}]}{[\text{REACTANTS}]} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

15.2 The Equilibrium Constant, K

Equilibrium Constants – Meaning of the Magnitude of K

K : $K >> 1$; $K << 1$; $K \approx 1$

$K >> 1$ $I_2(g) + Cl_2(g) \Longleftrightarrow 2\,ICl(g)$ $K = 2.1 \times 10^5$ @ 25°C

Product-favored reaction.

@ Equilibrium :- very little $I_2(g)$ and $Cl_2(g)$ remaining.

$K << 1$ $CH_3CO_2H(aq) + H_2O(l) \Longleftrightarrow CH_3CO_2^- + H_3O^+$ $K = 1.8 \times 10^{-5}$ @ 25°C

Reactant-favored reaction.

@ Equilibrium :- very little $CH_3CO_2^-$ and H_3O^+ produced.

$K \approx 1$ $2\,NO_2(g) \Longleftrightarrow N_2O_4(g)$ $K = 1.4$ @ 25°C

@ Equilibrium :- significant amounts of $NO_2(g)$ and $N_2O_4(g)$ present.

15.2 The Equilibrium Constant, K

Equilibrium Constants – Meaning of the Magnitude of K

The equilibrium constant, Kc, for the following reaction is 1.29×10^{-6} at 600 K.

$$COCl_2(g) \Leftrightarrow CO(g) + Cl_2(g)$$

Assuming that you start with only $COCl_2$, describe the relative abundance of each species present at equilibrium.

$[COCl_2(g)]$	a. Higher ✓	b. Lower	c. Can't tell
$[CO(g)]$	a. Higher	b. Lower ✓	c. Can't tell

$K = \underline{1.29 \times 10^{-6}}$ @ 600K

↳ Reactant-favored reaction.

15.2 The Equilibrium Constant, K

Writing Equilibrium Constant Expressions

$$aA + bB \Leftrightarrow cC + dD$$

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

However: a) Pure solids do not appear in the expression.

b) Pure liquids and solvents do not appear in the expression.

a) $C(s) + H_2O(g) \Leftrightarrow H_2(g) + CO(g)$ $$K = \frac{[H_2][CO]}{[H_2O]}$$

b) $CH_3CO_2H(aq) + H_2O(l) \Leftrightarrow CH_3CO_2^- + H_3O^+$ $$K = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]}$$

15.2 The Equilibrium Constant, K

The Relationship between K_p and K_c

$$2\ NOBr(g) \Longleftrightarrow 2\ NO(g) + Br_2(g)$$

$$K_c = \frac{[NO]^2[Br_2]}{[NOBr]^2} \quad ; \quad K_p = \frac{P_{NO}^2\ P_{Br_2}}{P^2_{NOBr}}$$

How are K_c and K_p related ?

$PV = nRT$

$P = \underline{(n/V)}\ RT$

$\hookrightarrow mol.\ell^{-1} = [\ ]RT$

$$K_p = \frac{P_{NO}^2\ P_{Br_2}}{P^2_{NOBr}}$$

$$= \frac{[NO]^2(RT)^2[Br_2](RT)}{[NOBr]^2(RT)^2}$$

$$= \frac{[NO]^2[Br_2]}{[NOBr]^2} \times \frac{(RT)^3}{(RT)^2}$$

$$K_p = K_c(RT)^3(RT)^{-2}$$

$$= K_c(RT)^{3-2}$$

$3 - 2$ = mol gas products - mol gas reactants

$2\ NO(g)$ & $Br_2(g)$ — $2\ NOBr$

$3 - 2$

$$\boxed{K_p = K_c(RT)^{\Delta n}}$$

Δn = mol of gas products - mol of gas reactants

15.2 The Equilibrium Constant, K

The Relationship between K_p and K_c

The equilibrium constant, **Kc**, for the following reaction is **2.90×10^{-2} at 1260 K**.
Calculate Kp for this reaction at this temperature.

$$2\,SO_3(g) \Leftrightarrow 2\,SO_2(g) + O_2(g)$$

$R = 0.0821\ L.atm.mol^{-1}.K^{-1}$

Kp = ?.00

a) 1
b) 2
c) 3 ✓
d) 4
e) 3

$$K_p = K_c\,(RT)^{\Delta n}$$

$$\Delta n = 2 + 1 - 2 = 1$$

$$K_p = 2.90\times10^{-2} \times (0.0821 \times 1260)$$
$$= 2.99$$