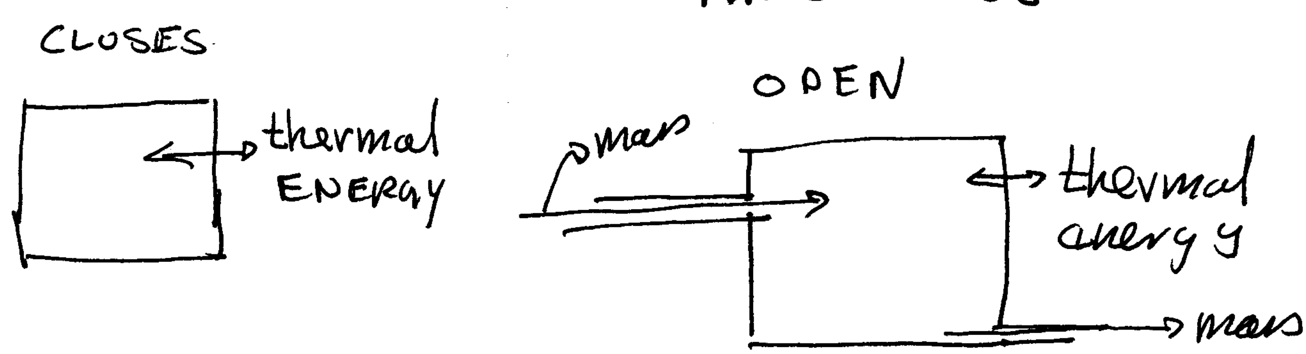
EQUILIBRIUM AND NONEQUILIBRIUM

<u>STEADY STATES</u> ARE REACHED WHEN THE SYSTEM'S OBSERVABLES (P, V, T, and CONC) DO NOT CHANGE IN TIME.

EQUILIBRIUM ⟷ CLOSED SYSTEM

NON EQUILIBRIUM ⟷ OPEN SYSTEM
→ INPUT AND OUTPUT MASS FLOWS



DEATH ⟷ EQUILIBRIUM

LIFE ⟷ OPEN
⟷ NONEQUILIBRIUM

Why is O_2 held so tightly in the lungs, then release so readily to myoglobin in the capillaries?

CONSIDER THE FOLLOWING GAS RXN:

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

FOR T AND V FIXED, FOR DIFFERENT INITIAL CONDITIONS WE GET THAT THE FOLLOWING RATIO IS A CONSTANT

$$\frac{P_{N_2O_4}}{P^2_{NO_2}} = K_p$$

IN THE CASE

$$[Co(H_2O)_6]^{2+} + 4\,Cl^-(aq) \rightleftharpoons [CoCl_4]^{2-} + 6H_2O(l)$$

PINK BLUE

$$\frac{[\text{tetrachloro}]}{[\text{hexaaqua}]\,[Cl^-]^4} = K_c$$

EMPIRICAL LAW

FOR ANY RXN

$$aA + bB \rightleftharpoons cC + dD$$

THE RATIO AT EQUILIBRIUM IS ALWAY THE SAME

$$K_c = \frac{[C]_{eq}^{c}\,[D]_{eq}^{d}}{[A]_{eq}^{a}\,[B]_{eq}^{b}} = \text{CONSTANT}$$

FOR GAS PHASE RXN

$$K_p = \frac{\left(P_C^{eq}\right)^c \left(P_D^{eq}\right)^d}{\left(P_A^{eq}\right)^a \left(P_B^{eq}\right)^b} \equiv \text{EQUILIBRIUM CONSTANT.}$$

LAW OF MASS ACTION (1864)

K_c AND K_p HAVE, IN GENERAL, DIMENSIONS

WE RATHER DEFINE A DIMENSIONLESS EQUILIBRIUM CONSTANT.

$$K = \frac{\left(P_C^{eq}/P_{ref}\right)^c \left(P_D^{eq}/P_{ref}\right)^d}{\left(P_A^{eq}/P_{ref}\right)^a \left(P_B^{eq}/P_{ref}\right)^b}$$

THERMODYNAMIC EQUILIBRIUM CONSTANT

$$K = \frac{\left([C]^{eq}/[ref]\right)^c \left([D]^{eq}/[ref]\right)^d}{\left([A]^{eq}/[ref]\right)^a \left([B]^{eq}/[ref]\right)^b}$$

WHERE WE HAVE SELECTED THE REFERENCE CONC. AND PRESSURE AS:

$$[ref] = 1 \ \frac{mol}{L}$$

$$P_{ref} = 1 \text{ atm}$$

LAW OF MASS ACTION: PURE SUBSTANCES AND MULTIPLE PHASES

① $H_2O(l) \rightleftharpoons H_2O(g)$ $\quad K_p = P_{H_2O}^{eq}$

P_{H_2O} IS INDEPENDENT OF THE AMOUNT OF LIQUID WATER.

② $CaCO(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_p = P_{CO_2}^{eq}$$

i) GASES → PARTIAL PRESSURES

ii) DISSOLVED SPECIES → CONC. IN mol/L

iii) PURE SOLIDS AND PURE LIQUIDS DO NOT APPEAR IN THE RATIO

HYDROLYSIS OF ETHYL ACETATE TO ACETIC ACID + ETHANOL

$$CH_3COOC_2H_3(aq) + H_2O(l)$$

$$\rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$$

$$K_c = \frac{[CH_3COOH][C_2H_5OH]}{[CH_3COOC_2H_3]}$$

FROM NOW ON WE ARE GOING TO USE THE THERMODYNAMIC EQUILIBRIUM CONSTANT BY USING CONC. AND PRESSURES RELATIVE TO THE REFERENCE PRESSURE (1 atm) AND CONC. (1 mol/L)

REVERSE RXN.

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \qquad K = \frac{(P^e_{H_2O})^2}{(P^e_{H_2})^2 (P^e_{O_2})}$$

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g) \qquad K_1' = \frac{1}{K_p}$$

EQUIVALENT OVERALL RXN

$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g) \qquad K'' = \sqrt{K_p}$$

SUM OF RXN

$$2BrCl(g) \rightleftharpoons Cl_2(g) + \cancel{Br_2(g)} \qquad K_1 = \frac{P^e_{Cl_2} P^e_{Br_2}}{P^{e\,2}_{BrCl}}$$

$$\cancel{Br_2(g)} + I_2(g) \rightleftharpoons 2IBr(g) \qquad K_2 = \frac{(P^e_{IBr})^2}{P^e_{Br_2} P^e_{I_2}}$$

$$2BrCl(g) + I_2(g) \rightleftharpoons Cl_2(g) + 2IBr(g)$$

$$K_3 = K_1 K_2$$