5) FIRST ORDER REVERSIBLE SINGLE REACTION

$$A \rightleftharpoons B$$

"REVERSIBLE" = BOTH FORWARD AND REVERSE REACTION OCCUR APPRECIABLY

REACTION #1
FORWARD POSITIVE
REVERSE NEGATIVE

$$R_A = \frac{dc_A}{dt} = \underbrace{-k_1 C_A}_{\text{DECREASE IN "A" DUE TO FORWARD RXN}} + \underbrace{k_{-1} C_B}_{\text{INCREASE IN "A" DUE TO REVERSE RXN}}$$

REVERSE IS PROPORTIONAL TO CONC. OF B

A REVERSIBLE REACTION WILL PROCEED TOWARD EQUILIBRIUM. AT EQUILIBRIUM, THE RATE OF CHANGE IN THE CONCENTRATIONS OF A & B WILL BE ZERO (IN A CLOSED SYSTEM). THUS $R_A = 0$ AND

$$0 = -k_1 C_{Aeq} + k_{-1} C_{Beq}$$

$$\boxed{\frac{k_1}{k_{-1}} = \frac{C_{Beq}}{C_{Aeq}} \equiv K_{EQ}}$$

EQUILIBRIUM CONSTANT

NOTE THAT k_1 & k_{-1} ARE FUNCTIONS OF TEMPERATURE SO $K_{EQ} = f(T)$ BUT LESS SO.

SOLVE DIFF. EQN USING FRACTIONAL CONVERSIONS...

$$C_A = C_{A0}(1 - x_A)$$

$$C_B = C_{B0}(1 - x_B)$$

$$-C_{A0}\frac{dx_A}{dt} = -k_1\left[C_{A0}(1 - x_A)\right] + k_{-1}\left[C_{B0}(1 - x_B)\right]$$

FIND RELATIONSHIP BETWEEN x_A & x_B:

$$A \rightleftharpoons B$$

NUMBER OF MOLES OF "A" WHICH HAVE REACTED = NUMBER OF MOLES OF "B" WHICH HAVE FORMED

$$n_{A0} - n_A = n_B - n_{B0}$$

$$C_{A0} - C_A = C_B - C_{B0}$$

$$C_{A0} - C_{A0}(1 - X_A) = C_{B0}(1 - X_B) - C_{B0}$$

$$C_{A0}[1 - 1 + X_A] = C_{B0}[1 - X_B - 1]$$

$$\underline{\underline{C_{A0} X_A = -C_{B0} X_B}}$$

FROM PREVIOUS SLIDE $\longrightarrow$ $$-C_{A0}\frac{dX_A}{dt} = -k_1 C_{A0}(1 - X_A) + k_{-1}(C_{B0} - C_{B0} X_B)$$

$$\frac{dx_A}{dt} = k_1(1-x_A) - k_{-1}\left(\frac{C_{B0}}{C_{A0}} + x_A\right)$$

let $\gamma = \frac{C_{B0}}{C_{A0}}$

$$\frac{dx_A}{dt} = k_1(1-x_A) - k_{-1}(\gamma + x_A)$$ ← DURING COURSE OF REACTION

AT EQUILIBRIUM $\quad x_A = x_{AEQ}$ & $\frac{dx_A}{dt} = 0$

$$0 = k_1(1-x_{AEQ}) - k_{-1}(\gamma + x_{AEQ})$$ ← AT EQUILIBRIUM

SOLVE FOR $K_{EQ} = \frac{k_1}{k_{-1}} = \frac{\gamma + X_{AEQ}}{1 - X_{AEQ}}$

SOLVE FOR $X_{AEQ} = \frac{K_{EQ} - \gamma}{K_{EQ} - 1}$

NOTE: X_{AEQ} IS THE FRACTIONAL CONVERSION AT EQUILIBRIUM... THE REACTION WILL NOT PROCEED TO "COMPLETION" ($X_A \rightarrow 1$). IT WILL PROCEED TO X_{AEQ}.

HOW TO SOLVE THE DIFF. EQN: WANT TO TAKE ADVANTAGE OF OUR KNOWLEDGE ABOUT EQUILIBRIUM.

DIFF EQN GENERAL − "DIFF EQN" AT EQUIL

$$\frac{dx_A}{dt} - 0 = \left[k_1(1-x_A) - k_{-1}(\gamma + x_A)\right] - \left[k_1(1-x_{AEQ}) - k_{-1}(\gamma + x_{AEQ})\right]$$

⋮ ALGEBRA

$$\frac{dX_A}{dt} = \frac{k_1(\gamma+1)}{\gamma + X_{AEQ}}(X_{AEQ} - X_A)$$

let $q = \frac{k_1(\gamma+1)}{\gamma + X_{AEQ}}$

$$\frac{dX_A}{dt} = q(X_{AEQ} - X_A)$$

$$\int_0^{X_A} \frac{dX_A}{(X_{AEQ} - X_A)} = q\int_0^t dt$$

$$-\ln\left[x_{AEQ}-x_A\right]\Big|_0^{x_A} = q\,t$$

$$-\ln\left[x_{AEQ}-x_A\right]+\ln\left[x_{AEQ}\right] = q\,t$$

$$\ln\left[\frac{x_{AEQ}-x_A}{x_{AEQ}}\right] = -q\,t$$

$$\boxed{x_A = x_{AEQ}\left(1-e^{-q\,t}\right)}$$

NOTE SIMILARITY TO RESULT OF FIRST ORDER IRREVERSIBLE!