

5) FIRST ORDER REVERSIBLE SINGLE REACTION



"REVERSIBLE" = BOTH FORWARD AND REVERSE REACTION OCCUR APPRECIABLY

$$R_A = \frac{dc_A}{dt}$$

$$= -k_1 C_A + k_{-1} C_B$$

DECREASE IN "A"
DUE TO FORWARD
RXN

INCREASE IN "A"
DUE TO REVERSE
RXN

REACTION #1
FORWARD POSITIVE
REVERSE NEGATIVE

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

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

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

EQUILIBRIUM
CONSTANT

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

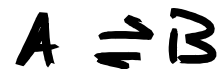
SOLVE DIFF. EQN USING FRACTIONAL CONVERSIONS...

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

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

$$-C_{A0} \frac{dX_A}{dt} = -k_1 [C_{A0}(1 - X_A)] + k_{-1} [C_{B0}(1 - X_B)]$$

FIND RELATIONSHIP BETWEEN X_A & X_B



NUMBER OF
MOLES OF "A"
WHICH HAVE
REACTED

=

NUMBER OF MOLES
OF "B" WHICH
HAVE FORMED

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

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

$$C_{A0} - C_{A0}(1 - \chi_A) = C_{B0}(1 - \chi_B) - C_{B0}$$

$$C_{A0}[1 - 1 + \chi_A] = C_{B0}[1 - \chi_B - 1]$$

$$\underline{\underline{C_{A0}\chi_A = -C_{B0}\chi_B}}$$

FROM
PREVIOUS
SLIDE

$$\rightarrow -C_{A0} \frac{d\chi_A}{dt} = -k_1 C_{A0}(1 - \chi_A) + k_1 (C_{B0} - C_{B0}\chi_B)$$

$$\frac{d\chi_A}{dt} = k_1 (1 - \chi_A) - k_{-1} \left(\frac{C_{B_0}}{C_{A_0}} + \chi_A \right)$$

let $\gamma = \frac{C_{B_0}}{C_{A_0}}$

$$\frac{d\chi_A}{dt} = k_1 (1 - \chi_A) - k_{-1} (\gamma + \chi_A) \quad \leftarrow \text{DURING COURSE OF REACTION}$$

AT EQUILIBRIUM $\chi_A = \chi_{A_{EQ}} \quad \& \quad \frac{d\chi_A}{dt} = 0$

$$0 = k_1 (1 - \chi_{A_{EQ}}) - k_{-1} (\gamma + \chi_{A_{EQ}}) \quad \leftarrow \text{AT EQUILIBRIUM}$$

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

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

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

How to solve the diff. eqn: want to take
advantage of our knowledge about equilibrium.

DIFF EQN — "DIFF EQN"
GENERAL — AT EQUIL

$$\frac{d\chi_A}{dt} - 0 = \left[k_1(1-\chi_A) - k_{-1}(\gamma + \chi_A) \right] -$$
$$\left[k_1(1-\chi_{A\text{EQ}}) - k_{-1}(\gamma + \chi_{A\text{EQ}}) \right]$$

⋮
ALGEBRA

$$\frac{d\chi_A}{dt} = \frac{k_1(\gamma+1)}{\gamma + \chi_{A\text{EQ}}} (\chi_{A\text{EQ}} - \chi_A)$$

let $q = \frac{k_1(\gamma+1)}{\gamma + \chi_{A\text{EQ}}}$

$$\frac{d\chi_A}{dt} = q (\chi_{A\text{EQ}} - \chi_A)$$

$$\int_0^{\chi_A} \frac{d\chi_A}{(\chi_{A\text{EQ}} - \chi_A)} = q \int_0^t dt$$

$$-\ln[\chi_{A\text{EQ}} - \chi_A] \Big|_0^{\chi_A} = q t$$

$$-\ln[\chi_{A\text{EQ}} - \chi_A] + \ln[\chi_{A\text{EQ}}] = q t$$

$$\ln \left[\frac{\chi_{A\text{EQ}} - \chi_A}{\chi_{A\text{EQ}}} \right] = -q t$$

$$\chi_A = \chi_{A\text{EQ}} (1 - e^{-q t})$$

NOTE
SIMILARITY
TO RESULT OF
FIRST ORDER
IRREVERSIBLE!