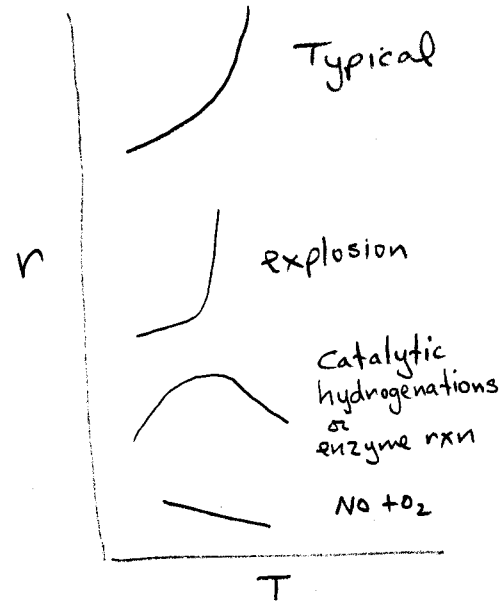


Rate Expressions - (algebraic equations)

$$r_A = - f(T) f(\text{concentration})$$



most common expression for  $f(T)$   
Arrhenius

Correlation

$$k = A \exp(-E/RT)$$

fraction of all collisions that have energy greater than E

only molecules that possess an energy greater than E will react

$k$  - rate "constant"

$A$  - preexponential factor

$R$  - 8.314 J/molK or 1.987 cal/molK

$T$  - K (absolute Temperature)

Arrhenius expression fails

1. Some free radical reactions - with low E
2. Large changes in temperature

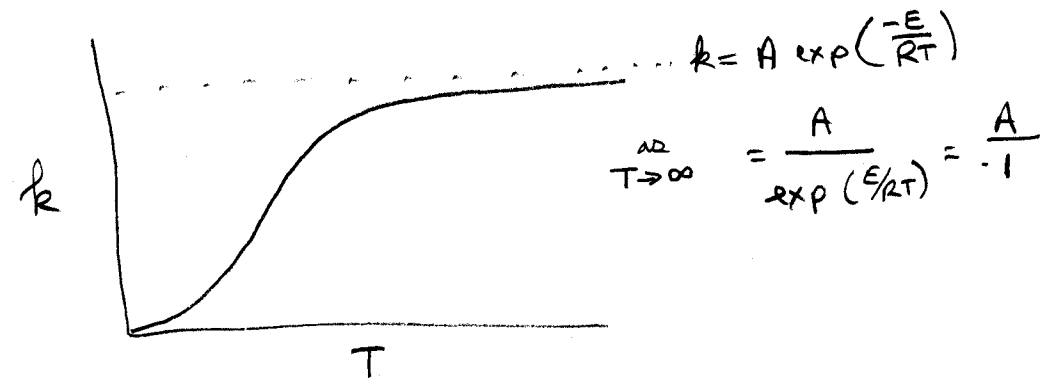
collision theory:  $k = B T^{1/2} e^{-E/RT}$  G-10

Transition state theory:  $k = C T e^{-E/RT}$  G-22

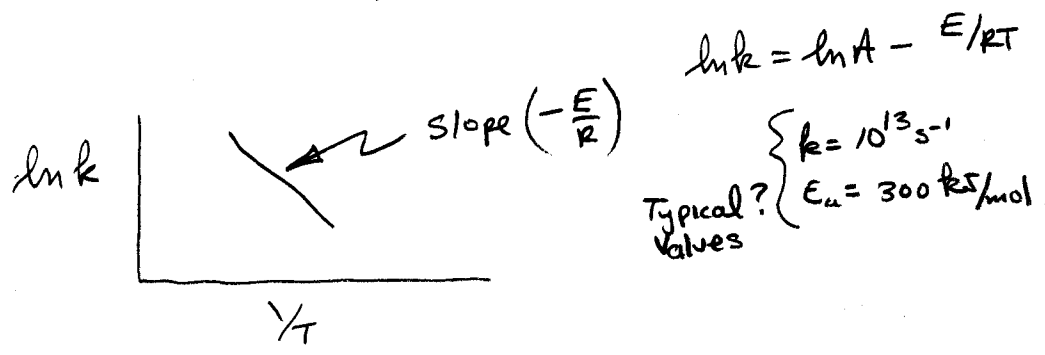
See Appendix G

Empirical expression  $k = D T^m e^{-E/RT}$

Arrhenius



Determination of Activation Energy



See comment on page 72: if increasing T by 10°C doubles the rate what is  $E_a$ ?

Reaction ORDER

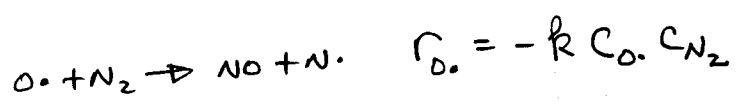
$$r = k C_A^\alpha C_B^\beta$$

(Power law expression)

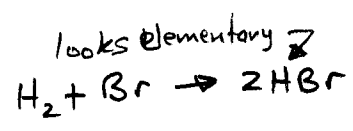
$\alpha$  order with respect to A  
 $\beta$  order with respect to B  
 overall rxn order  $\alpha + \beta$

Elementary Reactions - Irreducible reaction between chemical species.

Reaction order of each species is equal to the stoichiometric coefficient

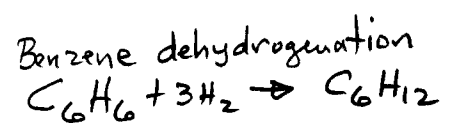


Non elementary



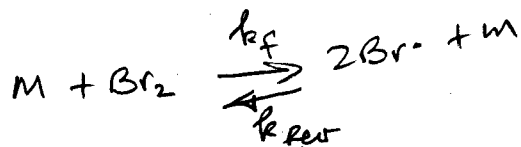
$$r_{HBr} = \frac{k_{exp} [H_2][Br_2]^{1/2}}{1 + K_{exp} [HBr]/[Br_2]}$$

See p 349



$$r = \frac{k_{exp} P_{H_2}^3 P_{benzene}}{(1 + K_{H_2} P_{H_2} + K_{benzene} P_{benzene})^4}$$

## Reversible reactions



$$r_{Br_2} = -k_f [M][Br_2] + k_{rev} [M][Br\cdot]^2$$

$$r_{forward} = -k_f [M][Br_2]$$

$$r_{reverse} = k_{rev} [M][Br\cdot]^2$$

$$-r_f = r_r \text{ at } \underline{\text{equilibrium!}}$$

Definition

Equilibrium (chemical)  $\leftarrow$  Concentration coefficient

$$K_{eqc} \equiv \frac{k_f}{k_r} = \frac{[M][Br\cdot]^2}{[M][Br_2]}$$

$$K_c \neq K_p$$

See on page 818 Appendix C  
929

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

$$\Delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

Add  $10^\circ\text{C}$  and you double the rate?

$$r_1 = k_1 C \quad \text{at } T_1$$

$$r_2 = k_2 C \quad \text{at } T_2 = T_1 + 10^\circ\text{C}$$

$$\text{Set } r_2 = 2r_1$$

find  $T_1$  at a given  $E_a$

$$\frac{r_1}{r_2} = \frac{k_1 C}{k_2 C} = \frac{A \exp(-E_a/RT_1)}{A \exp(-E_a/RT_2)}$$

$$\frac{r_1}{2r_1} = e^{-E_a/RT_1 + E_a/RT_2}$$

$$\ln\left(\frac{1}{2}\right) = \frac{E_a}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] = \frac{E_a}{R} \left[ \frac{1}{T_1 + 10\text{K}} - \frac{1}{T_1} \right]$$

$$-\frac{R}{E_a} \ln(0.5) = \left( \frac{1}{T_1} - \frac{1}{T_1 + 10} \right)$$

let's be lazy and use the root finder!

$$R = 8.314 \text{ J/(mol K)}$$

$$E_a = 300 \times 10^3 \text{ J/mol}$$

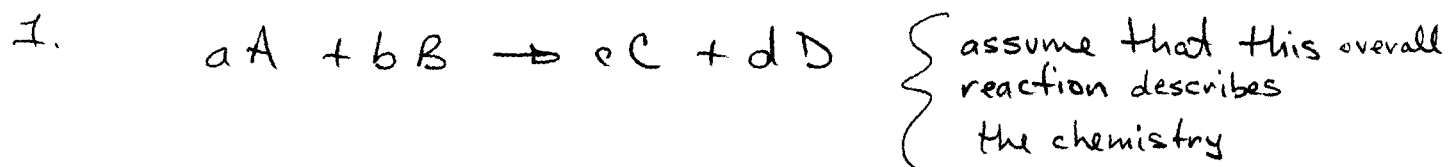
$$\text{Solving for } \boxed{T_1 = 728\text{K}}$$

This is hot

$$\text{check: } -\frac{8.314 \text{ J/mol K}}{300 \times 10^3 \text{ J/mol}} \ln(0.5) - \left( \frac{1}{728} - \frac{1}{738} \right) = 6 \times 10^{-7} \text{ K}$$



## Section 3.5 Stoichiometric Table



Look at reaction rates:

$$\begin{aligned} r_A &= ? r_B & \Rightarrow & r_A = \frac{a}{b} r_B \left[ = \frac{a \text{ mol A react}}{b \text{ mol B react}} \frac{\text{mol B}}{\text{m}^3 \text{ s}} \right] \\ \frac{\text{mol A}}{\text{m}^3 \text{ s}} & & \Rightarrow & r_A = -\frac{a}{c} r_C \\ & & & r_A = -\frac{a}{d} r_D \end{aligned}$$

$$\therefore r_A = \frac{a}{b} r_B = -\frac{a}{c} r_C = -\frac{a}{d} r_D$$

Stoic Table  $\rightarrow$  usefull if you want to define the reaction in terms of conversion - overall reaction

step 1. Define limiting concentration



look at initial concentrations or molar flow rates  
(Batch) (Flow)

CASE 1  $F_{A_0} = 20 \text{ mol/s}$   $F_{B_0} = 15 \text{ mol/s}$   $F_{A_0} = F_{B_0} \frac{a}{b} = (15 \frac{\text{mol B}}{\text{s}}) \left( \frac{2 \text{ mol A}}{3 \text{ mol B}} \right)$

$$= 10 \text{ mol A/s}$$

you need

$\therefore$  A is in excess of  
Stoichiometric  $x_A|_{\text{max}} = \frac{20 - 10}{20} = \frac{1}{2}$

USE  $x_B$   $x_B|_{\text{max}} = 1.0$

B is limiting Reagent

CASE 2

$$F_{A0} = 5 \text{ mol/s} \quad F_{B0} = 15 \text{ mol/s}$$

$$F_{A0} = (15 \text{ mol/s}) \frac{2 \text{ mol A}}{3 \text{ mol B}} = 10 \text{ mol A/s} \quad \text{we only have 5}$$

So only 7.5 mols of B/s will react

A limits  $X_A|_{\max} = 1$

$$X_B|_{\max} = \frac{15 - 7.5}{15} = \frac{1}{2}$$

Stoichiometric Table  $\rightarrow$  1) good for overall reactions  
 2) "molar changes  
 3) "Volume changes

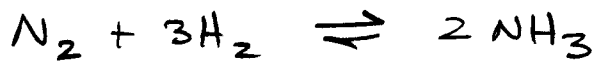
- Given { 1)  $aA + bB \rightarrow cC + dD$  Batch  $\rightarrow N$   
 2) diluted with inerts, I. Flow  $\rightarrow F$   
 3) limiting species A -  $X_A = \frac{F_{A0} - F_A}{F_{A0}} \equiv \frac{\text{mols A React}}{\text{mols A fed}}$

| Species  | Initial                    | molar change                 | Final                                   |
|----------|----------------------------|------------------------------|---|
| A        | $F_{A0}$                   | $-F_{A0} X_A$                | $F_A = F_{A0} - F_{A0} X_A$             |
| B        | $F_{B0}$                   | $-F_{A0} X_A \frac{b}{a}$    | $F_B = F_{B0} - \frac{b}{a} F_{A0} X_A$ |
| C        | $F_{C0}$                   | $+F_{A0} X_A \frac{c}{a}$    | $F_C = F_{C0} + \frac{c}{a} F_{A0} X_A$ |
| D        | $F_{D0}$                   | $+ (F_{A0} X_A) \frac{d}{a}$ | $F_D = F_{D0} + \frac{d}{a} F_{A0} X_A$ |
| <u>I</u> | <u><math>F_{I0}</math></u> | + 0                          | $F_I = F_{I0}$                          |
|          | $F_{T0} = \sum F_{i0}$     |                              |   |

$$F_T = \sum F_L = F_{T0} + F_{A0} X_A \left[ \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right]$$

Check units  
 $\left( \frac{F_B}{\text{that reacts}} \right) = F_{A0} X_A \frac{b}{a} = \text{mol A fed} \frac{\text{mol A React}}{\text{mol A fed}} \frac{\text{mol b React}}{\text{mol a React}}$

Book does not add subscript (I do!!)



$\Delta$  in # of moles  $4 \rightarrow 2$

Construct a stoic table:

| species    | initial   | change  | final                                 |
|------------|-----------|---|---------------------------------------|
| $N_2 (N)$  | $F_{N_0}$ | $- F_{N_0} \chi_N$  | $F_N = F_{N_0}(1 - \chi_N)$           |
| $H_2 (H)$  | $F_{H_0}$ | $- \frac{3 \text{ mol } H_2}{1 \text{ mol } N_2} F_{N_0} \chi_N$  | $F_{H_2} = F_{H_0} - 3F_{N_0} \chi_N$ |
| $NH_3 (A)$ | $F_{A_0}$ | $+ \frac{2 \text{ mol } NH_3}{1 \text{ mol } N_2} F_{N_0} \chi_N$ | $F_A = F_{A_0} + 2F_{N_0} \chi_N$     |
|            | $F_{T_0}$ | $- 2 F_{N_0} \chi_N$  | $F_T = \sum F_i$                      |

$$\textcircled{5} F_T = F_{T_0} - 2F_{N_0} \chi_N$$

if  $r_{N_2} = -k C_N C_H$

for PFR  $\frac{dF_N}{dV} = r_N = -k C_N C_H$

①

Since this is a single reaction  
solve using  $\chi$  or  $C$ 's

If this involved multiple reactions do not  
use  $\chi$ .

Look at both  
first use  $C$ 's

$$\chi_N = \frac{F_{N_0} - F_N}{F_{N_0}}$$

$$d\chi_N = 1 - \frac{dF_N}{F_{N_0}}$$

$$dF_N = -F_{N_0} d\chi_N$$

$$C_N = \frac{F_N}{v} = \frac{F_{N_0}(1 - X_N)}{v} \quad (2)$$

$$C_H = \frac{F_H}{v} = \frac{F_{H_0} - 3F_{N_0}X_N}{v} \quad (3)$$

what about  $v$  it is not constant since we have a  $\Delta N$  (moles)

Ideal gas law  $P_T v = F_T R T$

Ideal gas law at entrance  $P_{T_0} v_0 = F_{T_0} R T_0$

$$\frac{v}{v_0} = \frac{F_T T P_{T_0}}{F_{T_0} T_0 P_T} N_0 \quad (4)$$

until chapter 8:  $T = T_0$

until chapter 4.4  $P = P_0 \quad \Delta P = 0$

Solve using Polymath need

$F_{N_0}, F_{H_0}, F_{A_0}$   
 $k, v_0$  and  
 Volume of reactor  
 to find  $X_N$

Now find analytical

$$v = \frac{(F_{T_0} - 2F_{N_0}X_N)v_0}{F_{T_0}}$$

$$C_N = \frac{F_N}{v} = \frac{F_{N_0}(1 - X_N)F_{T_0}}{(F_{T_0} - 2F_{N_0}X_N)v_0}$$

$$C_H = \frac{F_H}{v} = \frac{(F_{H_0} - 3F_{N_0}X_N)F_{T_0}}{(F_{T_0} - 2F_{N_0}X_N)v_0}$$



$$-F_{N_0} \frac{dX_N}{dV} = -k \frac{F_{H_0} F_{N_0} F_{T_0}^2 (1-X_N) \left(1 - 3 \frac{F_{N_0}}{F_{H_0}} X_N\right)}{v_0^2 (F_{T_0} - 2 F_{N_0} X_N)^2}$$

$$-\frac{dX_N}{dV} = -k \frac{F_{H_0} F_{T_0}^2 (1-X_N) \left(1 - 3 \frac{F_{N_0}}{F_{H_0}} X_N\right)}{v_0^2 F_{T_0}^2 \left(1 - 2 \frac{F_{N_0}}{F_{T_0}} X_N\right)^2}$$

$\frac{m^3}{mol \cdot s}$

$r = -rc^2$

$$\left(\frac{m^3}{mol \cdot s}\right) \left(\frac{mol}{m^3}\right)^2 [=] \frac{mol}{m^3 \cdot s} \quad \frac{\frac{m^3}{mol} \cdot \frac{mol}{s} \cdot \frac{s}{m^3} \cdot \frac{s}{m^3}}{m^3} = \frac{1}{m^3}$$

$$\int dV = \frac{\left(1 - 2 \left(\frac{F_{N_0}}{F_{T_0}}\right) X_N\right)^2 v_0^2}{(1-X_N) \left(1 - 3 \frac{F_{N_0}}{F_{H_0}} X_N\right) F_{H_0}}$$

if  $3F_{N_0} = F_{H_0}$  Stoichiometric feed  $N_2 + 3H_2 \rightarrow 2NH_3$

$$\frac{1}{2} = 2 \left(\frac{F_{N_0}}{4F_{N_0}}\right) = \frac{1}{2}$$

$$\int dV = \int \frac{\left(1 - \frac{1}{2} X_N\right)^2 v_0^2}{(1-X_N)(1-X_N) F_{H_0}}$$

this is  $\epsilon = -1/2$  use equation A-6

$$\int_0^X \frac{(1+\epsilon x)^2}{(1-x)^2} dx = 2\epsilon(1+\epsilon) \ln(1-x) + \epsilon^2 x + \frac{(1+\epsilon)^2 x}{1-x}$$

