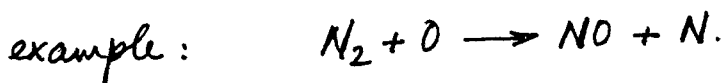
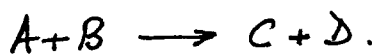


# Reactive Collisions

Reactive collisions  $\Leftrightarrow$  chemical identity changes



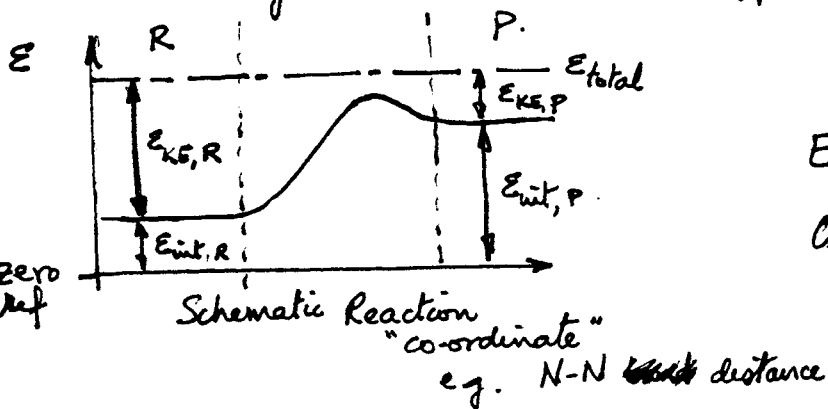
Reactive collisions are inelastic in general

$\Rightarrow$  (Internal energy)<sub>products</sub>  $\neq$  (Internal energy)<sub>reactants</sub>

$$(E_{int})_P \neq (E_{int})_R.$$

Endoergic reactions:  $(E_{int})_P > (E_{int})_R \Leftrightarrow (E_{KE})_P < (E_{KE})_R$

Exoergic reactions:  $(E_{int})_P < (E_{int})_R \Leftrightarrow (E_{KE})_P > (E_{KE})_R$



Endoergic reaction

Old-fashioned terminology:

- endothermic

$$E_{KE} = \frac{1}{2} m^* \bar{g}^2$$

For endoergic reactions  $\frac{1}{2} m_P^* \bar{g}'^2 = (E_{KE})_P < (E_{KE})_R = \frac{1}{2} m_R^* \bar{g}^2$

Hence after many reactive collisions  $\bar{g}^2$  falls  $\Leftrightarrow T$  falls  
unless there is an external energy supply to the gas mix  
 $\uparrow$  (heat)

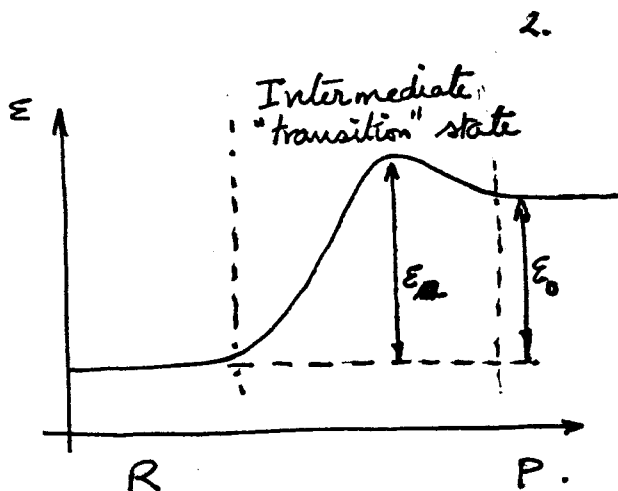
Converse for exoergic reactions

Endoergic reaction

$$(E_{int})_P - (E_{int})_R \equiv E_0$$

For many reactions, an energy  $E_a > E_0$  is required for the reaction to proceed,

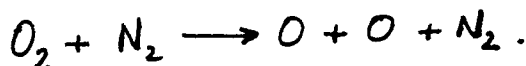
i.e. for chemical "bond" to be broken (and another one formed) sometimes



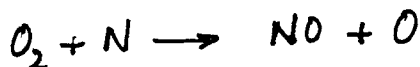
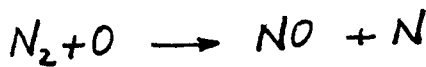
$E_a$  — activation energy. Clearly  $E_a \geq E_0$

Ex.

Simple "bond breaking"



Rearrangement



etc.

$Z_{AB}^{chem}$  — reactive collision rate:  $\frac{\# \text{ of reactive colls.}}{\text{time} \cdot \text{vol.}}$   $A+B \rightarrow C+D$

(Chemical) reaction cross-section  $\sigma_{AB \rightarrow CD} - \sigma^{chem}$  for short

$$Z_{AB}^{chem} = \frac{n_A n_B}{(1 + \delta_{AB})} \int_0^{\infty} g \sigma^{chem} N(g) dg$$

$$N(g) dg = \left( \frac{m_{AB}^*}{2\pi kT} \right)^{3/2} e^{-\frac{m_{AB}^* g^2}{2kT}} 4\pi g^2 dg$$

assuming gas in thermal equilibrium at temp T.

Comment on factor  $(1 + \delta_{AB})$  in  $Z_{AB}$

$$\delta_{AB} - \text{Kronecker delta} = \begin{cases} 1 & A=B \\ 0 & A \neq B \end{cases}$$

$$(1 + \delta_{AB}) - \text{symmetry factor} = \begin{cases} 2 & A=B \\ 1 & A \neq B \end{cases}$$

Origin of this factor.

Collision rate was obtained by considering  
A class  $C_i$  & B class  $Z_i$

then we integrated over all velocities  $C_i$  &  $Z_i$

Now if B is identical to A this will result in  
double counting.

cf.  $(C_i, Z_i) \rightarrow (C_i', Z_i')$  vs  $(Z_i, C_i) \rightarrow (Z_i', C_i')$   
 $\begin{matrix} A & B & & A & B \\ & & \swarrow & \searrow & \end{matrix}$   
 different collisions if  $B \neq A$ .

But  $(C_i, Z_i) \rightarrow (C_i', Z_i')$  vs  $(Z_i, C_i) \rightarrow (Z_i', C_i')$   
 $\begin{matrix} A & A & & A & A \\ & & \swarrow & \searrow & \end{matrix}$   
 same collision if  $B = A$

See Fig II-10 p 53 of text.

① Note: Suggest  $(1 + \delta_{AB})$  rather than  $\sigma$  for symmetry factor to avoid confusion with cross-sections.

② Note:  $\theta_{BA} = n_A \int_0^\infty g \sigma_{AB} \chi(g) dg$   
 $= \frac{(1 + \delta_{AB}) Z_{AB}}{n_B}$  ;  $Z_{AB} = \frac{n_A n_B}{(1 + \delta_{AB})} \int_0^\infty g \sigma_{AB} \chi(g) dg$

$\theta_{BA}$ : collision frequency of randomly chosen B molecule with A molecules

Endoergic reaction:

$$(E_{KE})_R = \frac{1}{2} m_A C^2 + \frac{1}{2} m_B Z^2 = \frac{1}{2} (m_A + m_B) G^2 + \frac{1}{2} m_{AB}^* g^2$$

$$(E_{KE})_P = \frac{1}{2} m_C C'^2 + \frac{1}{2} m_D Z'^2 = \frac{1}{2} (m_C + m_D) G'^2 + \frac{1}{2} m_{CD}^* g'^2$$

Now  $m_C + m_D = m_A + m_B$  Mass conservation

Momentum  $(m_C + m_D) G'_i = (m_A + m_B) G_i$  Momentum conservation  
 $\Rightarrow G'_i = G_i$

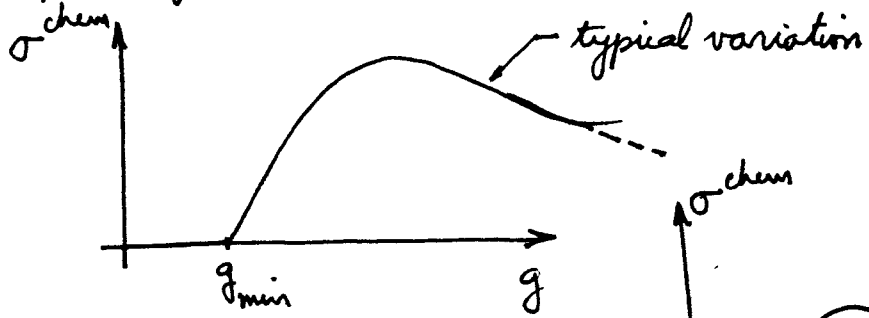
$$(E_{int})_R + (E_{KE})_R = (E_{int})_P + (E_{KE})_P$$

$$\Rightarrow (E_{KE})_R - (E_{KE})_P = (E_{int})_P - (E_{int})_R \equiv E_0$$

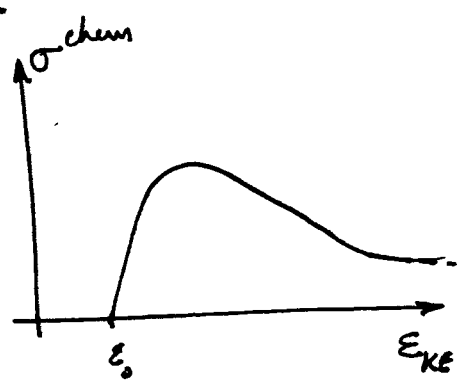
$$\frac{1}{2} m_{AB}^* g^2 - \frac{1}{2} m_{CD}^* g'^2 = E_0$$

Now smallest possible value  $g' = 0 \Rightarrow \frac{1}{2} m_{AB}^* g^2 \geq E_0$

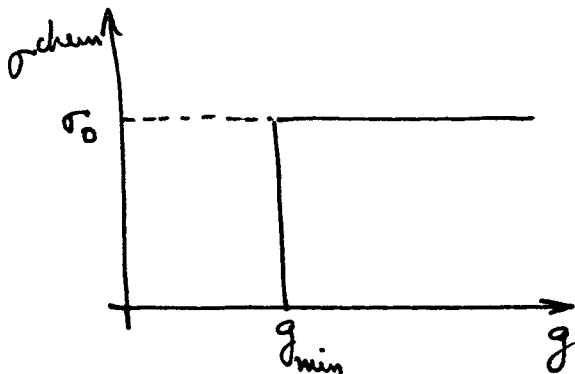
In fact if  $E_a > E_0$   $g'_{min} > 0$  &  $\frac{1}{2} m_{AB}^* g^2 \geq E_a$



$\sigma_{\neq}^{chem} = 0$  for  $g < g_{min}$   
 $g_{min} = \left( \frac{2 E_a}{m_{AB}^*} \right)^{1/2}$



Simplest model for  $\sigma^{\text{chem}}$



$$g_{\text{min}} = \left( \frac{2 \epsilon_a}{m_{AB}^*} \right)^{1/2}$$

For gas mix @ T

$$\begin{aligned} Z_{AB}^{\text{chem}} &= \frac{n_A n_B}{(1 + \delta_{AB})} \int_0^{\infty} g \sigma^{\text{chem}} \chi_H(g) dg \\ &= \frac{n_A n_B}{(1 + \delta_{AB})} \sigma_0 4\pi \left( \frac{m_{AB}^*}{2\pi kT} \right)^{3/2} \int_{g_{\text{min}}}^{\infty} g^3 e^{-\frac{m_{AB}^* g^2}{2kT}} dg \end{aligned}$$

$$\text{Let } \frac{m_{AB}^* g^2}{2kT} = x \quad g^2 = \frac{2kT}{m_{AB}^*} x$$

$$2g dg = \frac{2kT}{m_{AB}^*} dx$$

$$\int_{g_{\text{min}}}^{\infty} g^2 e^{-\frac{m_{AB}^* g^2}{2kT}} g dg = \int_{x_{\text{min}}}^{\infty} \left( \frac{2kT}{m_{AB}^*} \right) \left( \frac{kT}{m_{AB}^*} \right) x e^{-x} dx$$

$$= 2 \left( \frac{kT}{m_{AB}^*} \right)^2 \left\{ -x e^{-x} \Big|_{x_{\text{min}}}^{\infty} + \int_{x_{\text{min}}}^{\infty} e^{-x} dx \right\}$$

$$= 2 \left( \frac{kT}{m_{AB}^*} \right)^2 \left\{ +x_{\text{min}} e^{-x_{\text{min}}} + -e^{-x} \Big|_{x_{\text{min}}}^{\infty} \right\}$$

$$= 2 \left( \frac{kT}{m_{AB}^*} \right)^2 (1 + x_{\text{min}}) e^{-x_{\text{min}}}$$

$$x_{\text{min}} = \frac{m_{AB}^*}{2kT} g_{\text{min}}^2 = \frac{\epsilon_a}{kT}$$

$$\text{Finally } Z_{AB}^{\text{chem}} = \frac{n_A n_B}{(1 + \delta_{AB})} 4\sigma_0 \left( \frac{kT}{2\pi m_{AB}^*} \right)^{1/2} \left( 1 + \frac{\epsilon_a}{kT} \right) e^{-\epsilon_a/kT}$$

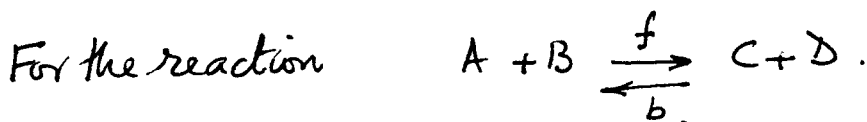
$$[Z_{AB}] = \frac{\text{(number of cells)}}{\text{vol. time}}$$

$$\text{If } E_a/k \gg T \quad \left( \frac{E_a}{kT} \gg 1 \right)$$

$$1 + \frac{E_a}{kT} \approx \frac{E_a}{kT}$$

$$\& z_{AB}^{\text{chem}} = n_A n_B \frac{4\sigma_0 E_a}{(1 + \delta_{AB})} \left( \frac{1}{2\pi m_{AB}^* kT} \right)^{1/2} e^{-E_a/kT}$$

$\uparrow$  weak T dependence       $\uparrow$  strong exponential T-dependence



(traditional) experimental observation for chemical reaction rate

$$-\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \frac{dn_C}{dt} = \dots = n_A n_B k_f - n_C n_D k_b$$

"forward" & "backward" are traditional terms rather than "direct" and "inverse"

Compare forward rate with  $z_{AB}^{\text{chem}}$

$$n_A n_B k_f \approx n_A n_B \frac{4\sigma_0 E_a}{(1 + \delta_{AB})} \left( \frac{1}{2\pi m_{AB}^* kT} \right)^{1/2} e^{-E_a/kT}$$

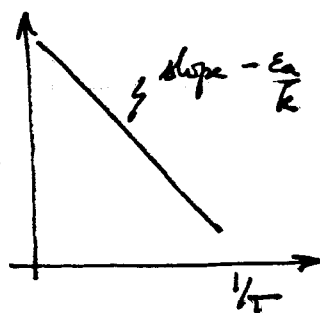
$$k_f \approx \frac{4\sigma_0 E_a}{(1 + \delta_{AB})} \cdot \left( \frac{1}{2\pi m_{AB}^* kT} \right)^{1/2} e^{-E_a/kT}$$

$$\approx A e^{-E_a/kT}$$

$\uparrow$  weak T dependence       $\uparrow$  strong T dependence       $\ln k$

$$\ln k_f = \ln A - E_a/kT$$

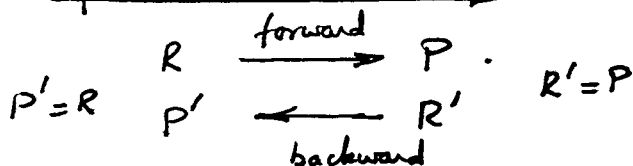
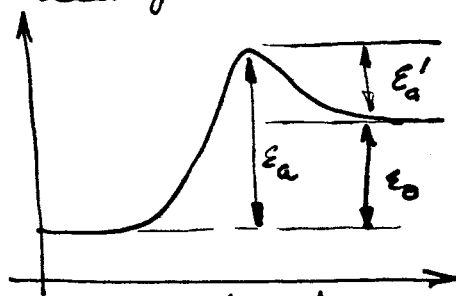
Arrhenius plot.



The backward (inverse) reaction of an endergonic reaction is exergonic

$$\text{i.e. } (\mathcal{E}_{\text{int}})_{P'} < (\mathcal{E}_{\text{int}})_{R'}$$

$$\mathcal{E}'_a = \mathcal{E}_a - \mathcal{E}_0$$



Proceeding as before

$$Z_{\text{CD}}^{\text{chem}} \approx \frac{n_C n_D 4\sigma_0' \mathcal{E}'_a}{(1 + \delta_{\text{CD}})} \left( \frac{1}{2\pi m_{\text{CD}}^* kT} \right)^{1/2} e^{-\frac{\mathcal{E}'_a}{kT}} = n_C n_D k_b$$

$$\& \text{ so } k_b \approx A' e^{-\mathcal{E}'_a/kT}$$

Now for chemical equilibrium

$$\frac{dn_s}{dt} = 0 \quad s = A, B, C, D.$$

Let equilibrium number densities be  $n_s^*$

$$\text{then } n_A^* n_B^* k_f - n_C^* n_D^* k_b = 0$$

$$\Rightarrow \frac{n_C^* n_D^*}{n_A^* n_B^*} = \frac{k_f}{k_b} \equiv K_{\text{eq}} \text{ "equilibrium constant"}$$

Our model shows

$$\frac{k_f}{k_b} = \frac{A e^{-\mathcal{E}_a/kT}}{A' e^{-\mathcal{E}'_a/kT}}$$

$$= \frac{A}{A'} e^{-(\mathcal{E}_a - \mathcal{E}'_a)/kT}$$

$$K_{\text{eq}} = \frac{k_f}{k_b} = \frac{A}{A'} e^{-\mathcal{E}_0/kT}$$