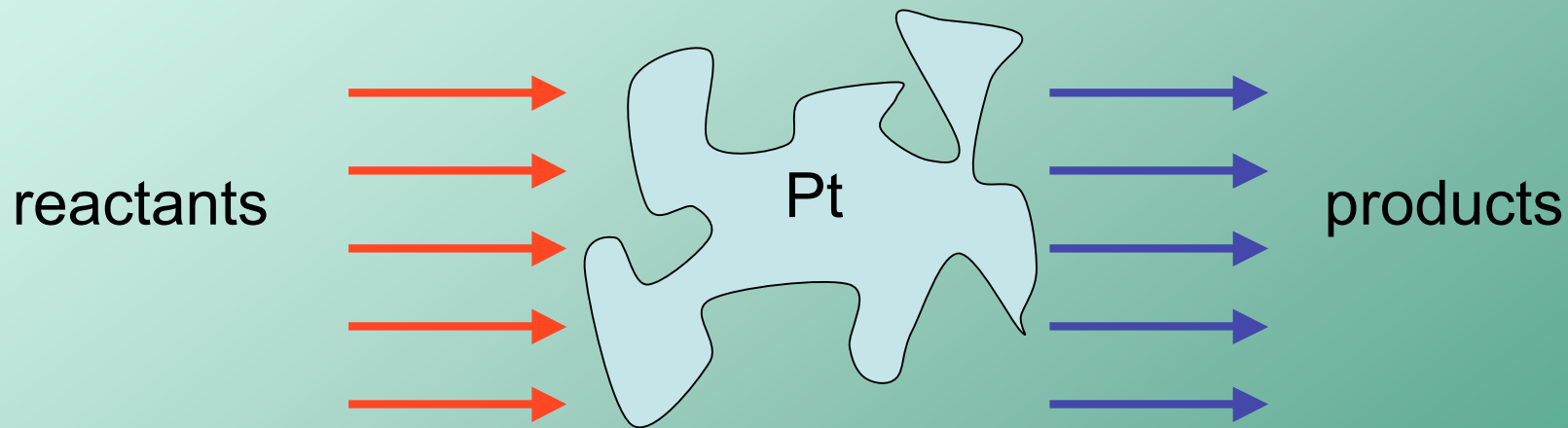
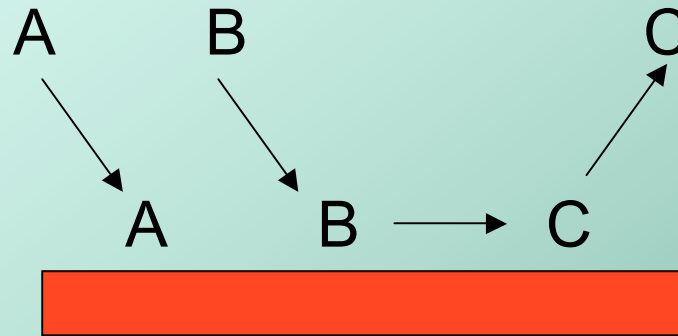


## 2. Kinetics in heterogeneous catalysis

- Measure dependence of rate on temperature and reactant pressures.
- Reflect conc. and kinetics of adsorbed species.

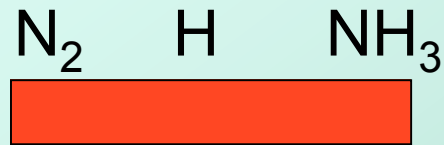
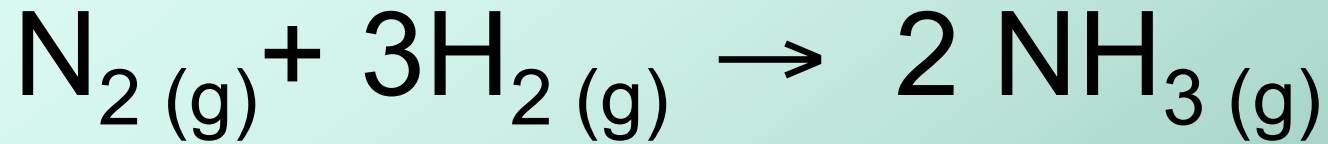


## a. Pressure dependence



- “Langmuir-Hinshelwood” mechanism
  - Reaction between co-adsorbed species
  - Most common route followed by catalytic processes

$$Rate = k\theta_A\theta_B$$



$$\theta_{\text{N}_2} = \frac{B_{\text{N}_2} p_{\text{N}_2}}{1 + B_{\text{H}_2} p_{\text{H}_2}^{1/2} + B_{\text{N}_2} p_{\text{N}_2} + B_{\text{NH}_3} p_{\text{NH}_3}}$$

$$\theta_{\text{H}} = \frac{B_{\text{H}_2} p_{\text{H}_2}^{1/2}}{1 + B_{\text{H}_2} p_{\text{H}_2}^{1/2} + B_{\text{N}_2} p_{\text{N}_2} + B_{\text{NH}_3} p_{\text{NH}_3}}$$

$$\text{Rate} = k^{\text{het}} \theta_{\text{N}_2} \theta_{\text{H}}$$

$$= \frac{k^{\text{het}} B_{\text{N}_2} p_{\text{N}_2} B_{\text{H}_2} p_{\text{H}_2}^{1/2}}{\left(1 + B_{\text{H}_2} p_{\text{H}_2}^{1/2} + B_{\text{N}_2} p_{\text{N}_2} + B_{\text{NH}_3} p_{\text{NH}_3}\right)^2}$$

Langmuir-Hinshelwood  
equation

- For many catalysts

NH<sub>3</sub> and N<sub>2</sub> adsorb very weakly  
i.e.

$$B_{NH_3} p_{NH_3}, B_{N_2} p_{N_2} \ll 1$$

H<sub>2</sub> adsorbs strongly  
i.e.

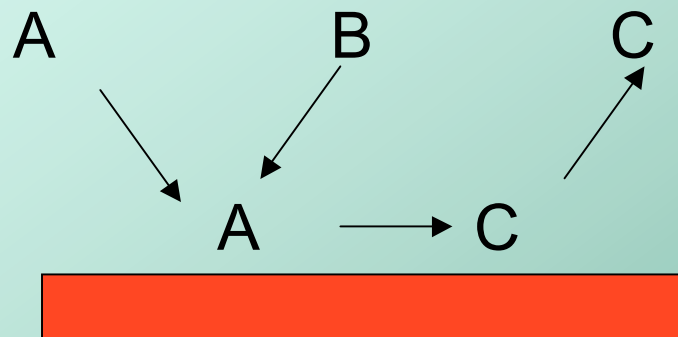
$$B_{H_2} p_{H_2}^{1/2} \gg 1$$

So L-H equation approximates to

$$Rate = \frac{k^{het} B_{N_2} p_{N_2}}{B_{H_2} p_{H_2}^{1/2}}$$

First order with respect to nitrogen, negative half order with respect to hydrogen

- “Eley-Rideal” mechanism
  - alternative reaction route - reaction between gas phase and adsorbed phase species
  - much less common than L-H

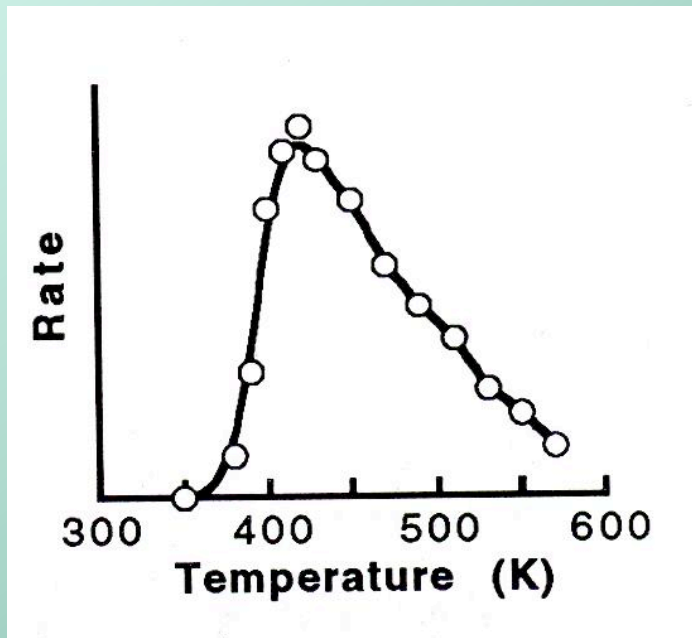


$$\begin{aligned}
 \text{Rate} &= k^{\text{het}} \theta_A p_B \\
 &= \frac{k^{\text{het}} B_A p_A p_B}{1 + B_A p_A}
 \end{aligned}$$

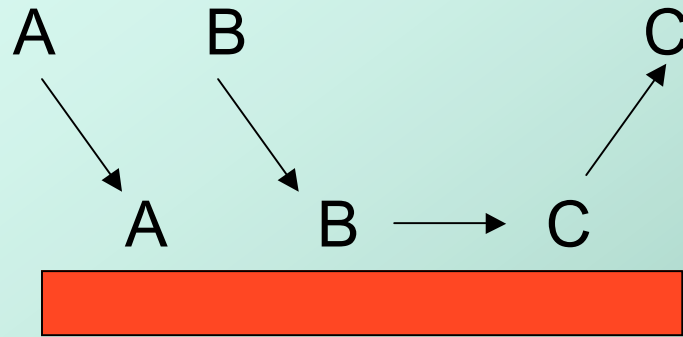
Weak ads. of A;  $\text{Rate} \propto p_A p_B$

Strong ads. of A;  $\text{Rate} \propto p_B$

- Temperature dependence
  - Often observe very strong deviations from Arrhenius behaviour
  - Rate increases at low T, but *decreases* at high T
  - Arises because need both vacant surface sites *and* adsorbed species for high rates



Catalytic oxidation of CO



- Assume A adsorbs strongly, B weakly
- Low T - rate limited by vacant sites

$$Rate = k^{het} (1 - \theta_A) = k^{het} \left( 1 - \frac{B_A p_A}{1 + B_A p_A} \right) \approx \frac{k^{het}}{B_A p_A}$$

$$k^{het} = A e^{-E_{react}/RT}$$

$$B_A = A' e^{|\Delta H_{ads}|/RT}$$

$$Rate = \frac{A''}{p_A} \left( e^{-\left( E_{react} + |\Delta H_{ads}| \right) / RT} \right)$$

$$E^{apparent} = E_{react} + |\Delta H_{ads}|$$

- High T, rate limited by the supply of A to the surface

$$Rate = k^{het} \theta_A = k^{het} \left( \frac{B_A p_A}{1 + B_A p_A} \right) \approx k^{het} B_A p_A$$

$$k^{het} = A e^{-E_{react}/RT}$$

$$B_A = A' e^{|\Delta H_{ads}|/RT}$$

$$Rate = A'' p_A \left( e^{-\left( E_{react} - |\Delta H_{ads}| \right) / RT} \right)$$

$$E^{apparent} = E_{react} - |\Delta H_{ads}|$$

- So activation energy drops from  $E_{react} + |\Delta H_{ads}|$  to  $E_{react} - |\Delta H_{ads}|$  as the temperature rises.



# Measurement of the heat of adsorption

- Physisorption vs chemisorption
- Models of the surface chemical bond
- Variations with surface coverage
- Understanding surface chemical processes
- Different approaches used, since none are universally applicable

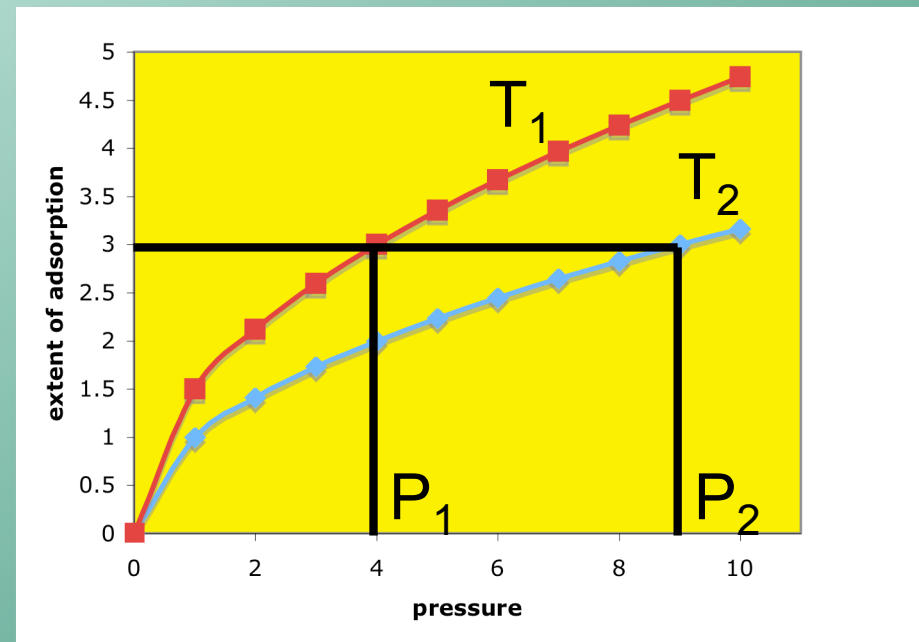
- Calorimetry

- Heat evolved =  $n_{\text{ads}} \times (-\Delta H_{\text{ads}})$
- Does't need "reversibility"
- Integral measurement
- Main problem is with  $n_{\text{ads}}$
- OK for powders etc but extremely hard to set up sufficiently sensitive measurements for macroscopic materials

- Determination of isosteres (P vs T at constant  $\theta$ )
  - Fit modified Clausius-Clapeyron eq.
  - Accurate determination of  $\Delta H_{ads}$  as  $f(\theta)$
  - Need thermodynamic reversibility - OK for physisorption, but often not for chemisorption

$$\left( \frac{\partial \ln p}{\partial T} \right)_{\theta} = - \frac{\Delta H_{ads}^{\theta}}{RT^2}$$

$$\left( \ln \frac{p_2}{p_1} \right)_{\theta} = \frac{\Delta H_{ads}^{\theta}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$



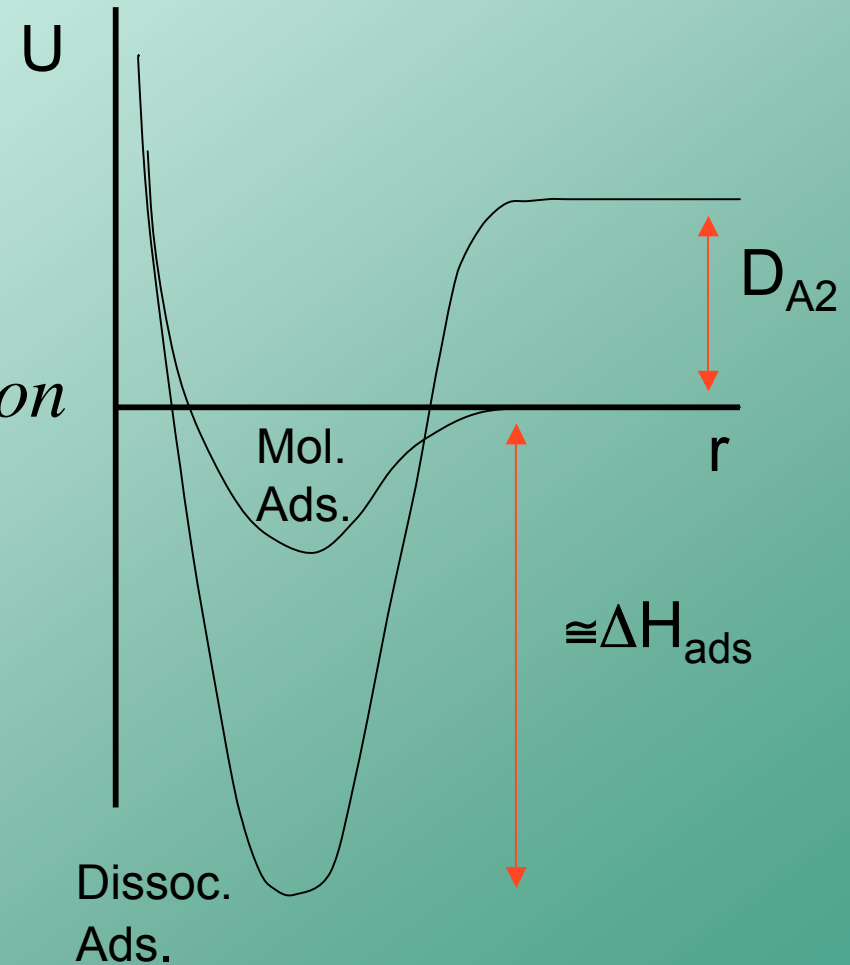
- Measure desorption kinetics

$$\Delta H \approx E_f^{act} - E_r^{act}$$

but  $E_{adsorption}^{act} = 0$  often for adsorption

$$\therefore |\Delta H_{ads}| \approx E_{desorption}^{act}$$

Main requirement -  
thermal -induced  
desorption must take  
place



# Experimental investigation of surfaces

- Three obstacles
  - Preservation of the integrity of the surface under investigation
  - The number of atoms at the surface ( $10^{15}$  atoms  $\text{cm}^{-2}$ )
  - The ratio of surface to bulk atoms ( $<10^{-7}$  for macroscopic samples)

# Preservation of the surface phase

- Gas molecules often react with unit probability at a solid surface.

$$Z = \frac{p}{(2\pi mkT)^{1/2}}$$

Z = gas flux ( $\text{m}^{-2} \text{s}^{-1}$ )

p = pressure ( $\text{Nm}^{-2}$ )

m = mass of a molecule (kg)

Pressure (bar)	Flux ( $\text{m}^{-2} \text{s}^{-1}$ , 28 amu, 300K)
1	$2.7 \times 10^{27}$
$10^{-9}$	$2.7 \times 10^{18}$
$10^{-13}$	$2.7 \times 10^{14}$

- Recall surfaces have around  $10^{19}$  atoms  $\text{m}^{-2}$
- So may need vacuums of around  $10^{-13}$  bar in “reactive systems”
- Termed “ultra-high vacuum”



Oxford “oxide MBE system”

# Achieving surface sensitivity

- $< 10^{15}$  atoms (per  $\text{cm}^{-2}$ ) i.e.  $10^{-9}$  moles,  $10^7$  less than in the bulk
- Sometimes can study “powders”, but not normally a valid route
- Need to employ techniques which are
  - Highly sensitive
  - Only “see” the surface
  - Termed “surface sensitive”