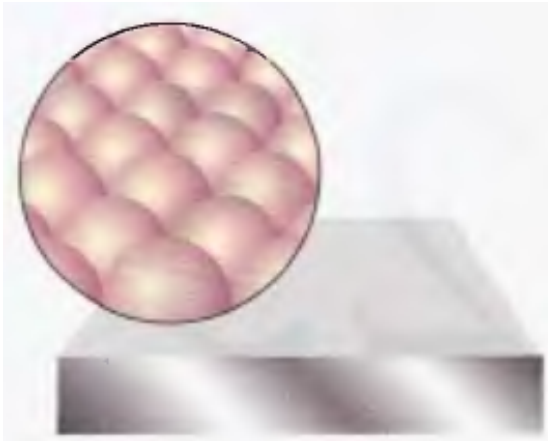
simple picture of a perfect crystal surface (flat)



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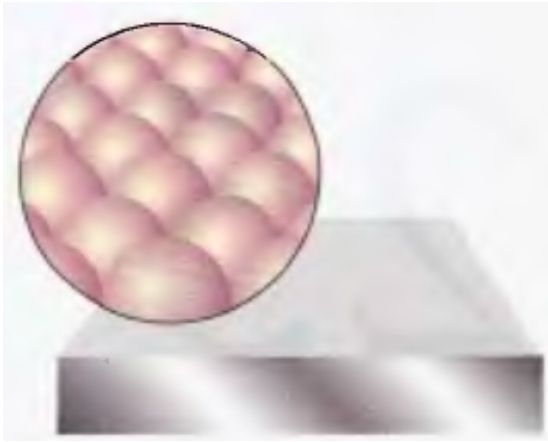
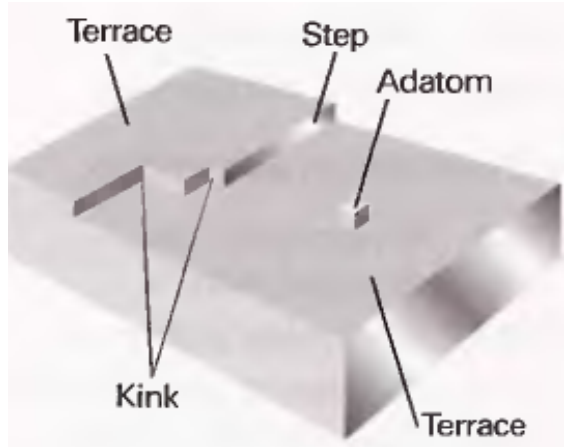
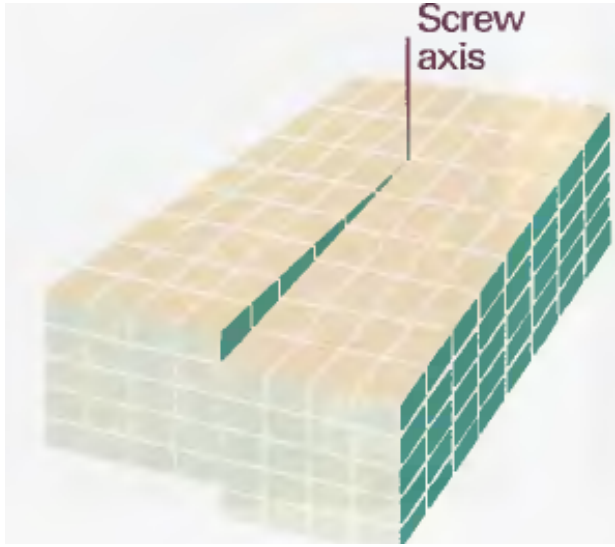


surface with defects





screw dislocation occurs where one region is pushed up through one or more unit cells relative to another region

The cut extends to the screw axis. As atoms lie along the step the dislocation rotates round the screw axis and is not annihilated

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material to which it adsorbs : adsorbent or substrate

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1 m^2 of metal surface has $\approx 10^{19}$ atoms
$\therefore$ each atom is struck about 10^8 times each second
Even if only a few collisions leave a molecule adsorbed to the surface, the time for which a freshly prepared surface remains clean is very short

Physisorption and chemisorption

Physisorption :

• long range, weak van der Waals interaction between adsorbate and substrate
• energy released on physisorption : $\mathcal{O}$(enthalpy of condensation)
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insufficient to lead to bond breaking, so a physisorbed molecule retains its identity, although it is distorted on surface

Adsorbate	$\Delta_{ad}H^{\ominus}$(kJ/mol)
CH_4	−21
H_2	−84
H_2O	−59
N_2	−21

data at 298K

Chemisorption : molecules/atoms stick to surface by forming a chemical bond, and tend to find sites that maximize their coordination number with the substrate

$\Delta H_{\text{chemisorption}} \gg \Delta H_{\text{physisorption}}$

distance between surface and closest adsorbate atom typically shorter for chemisorption than for physisorption

$\Delta_{ad} H^{\ominus}$(kJ/mol) data at 298K

Adsorbate	Adsorbent		
	Cr	Fe	Ni
C_2H_4	−427	−285	−243
CO	..	−192	..
H_2	−188	−134	..
NH_3	..	−188	−155

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Except in special cases, chemisorption must be exothermic

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•These adsorbates also show order–disorder transitions when they are heated enough for thermal motion to overcome the particle–particle interactions, but not so much that they are desorbed

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Define: fractional coverage, $\theta = \frac{\text{number of adsorption site soccupied}}{\text{number of adsorption sites available}}$

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or, $\theta = \frac{\alpha p}{1+\alpha p}$, where $\alpha = \frac{k_a}{k_d}$ (dimensions : 1/pressure)

Ex. : adsorption of CO on charcoal at 273 K

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0	93.3
V/cm^3	10.2	18.6	25.5	31.5	36.9	41.6	46.1

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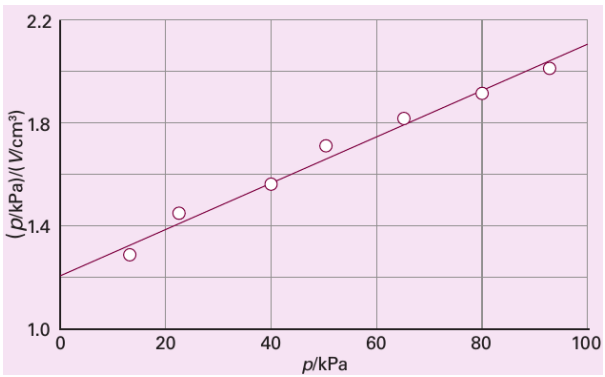

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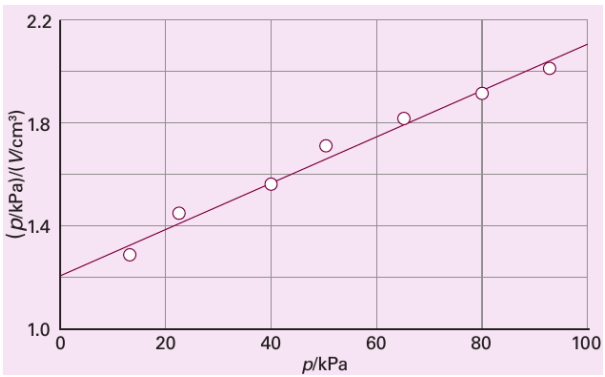

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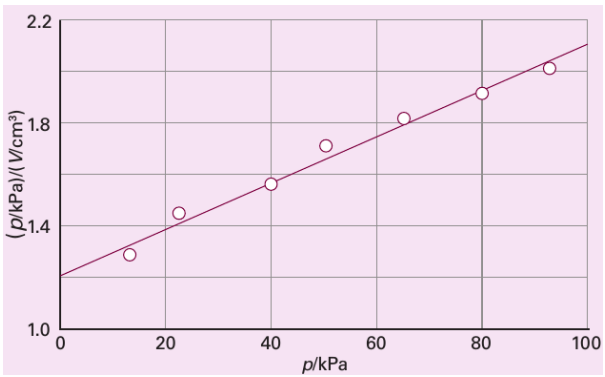

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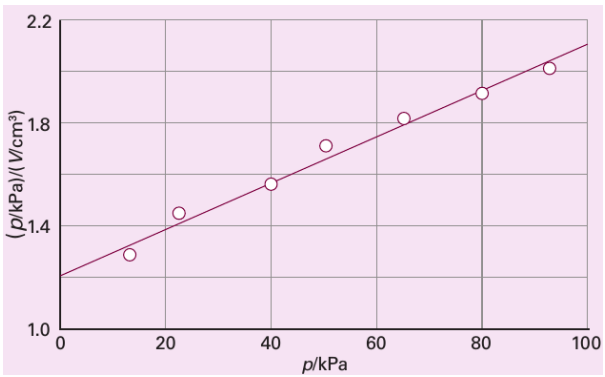


Ex. : adsorption of CO on charcoal at 273 K

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0	93.3
V/cm^3	10.2	18.6	25.5	31.5	36.9	41.6	46.1

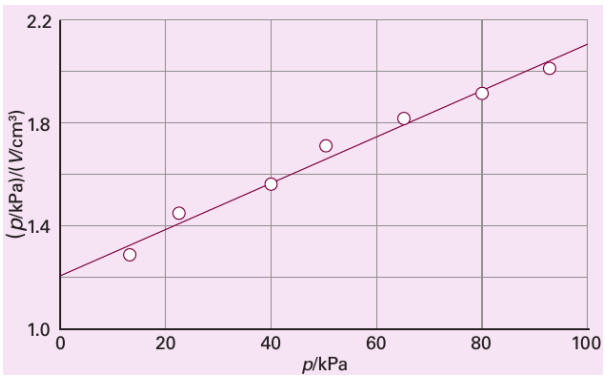
(V corrected to 1.00 atm and 273 K)

$$\theta = \frac{\alpha p}{1+\alpha p} \text{ or, } \alpha p = \alpha p\theta + \theta$$

write: $\theta = \frac{V}{V_\infty}$ and divide both sides by αV

then $\frac{p}{V} = \frac{p}{V_\infty} + \frac{1}{\alpha V_\infty}$

p/kPa	13.3	26.7	40.0	53.3	66.7	80.0	93.3
$\frac{p}{V}$	1.30	1.44	1.57	1.69	1.81	1.92	2.02



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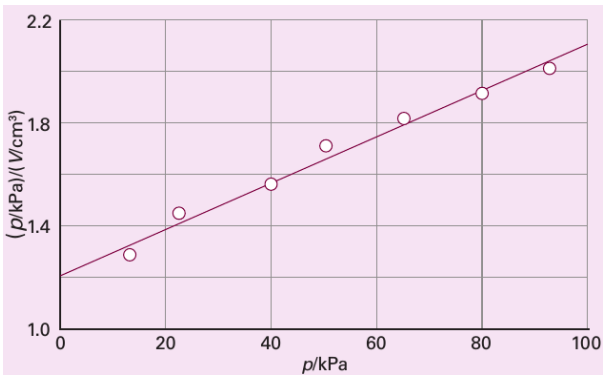

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volumes in definition of θ are those of the free gas measured under same conditions of temperature and pressure, not the volume the adsorbed gas occupies when attached to surface

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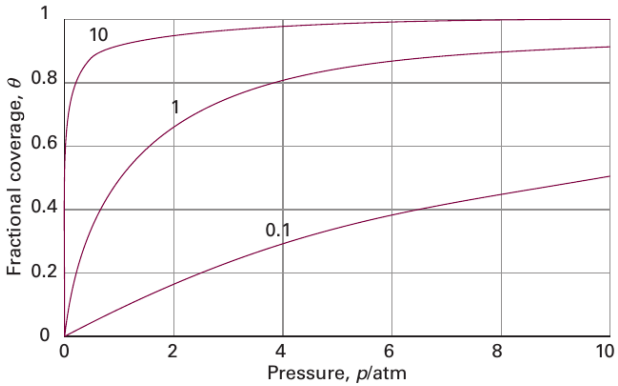
$$\text{Equilibrium: } \theta = \frac{\sqrt{\alpha p}}{1+\sqrt{\alpha p}},$$

surface coverage depends more weakly on pressure than for non-dissociative adsorption



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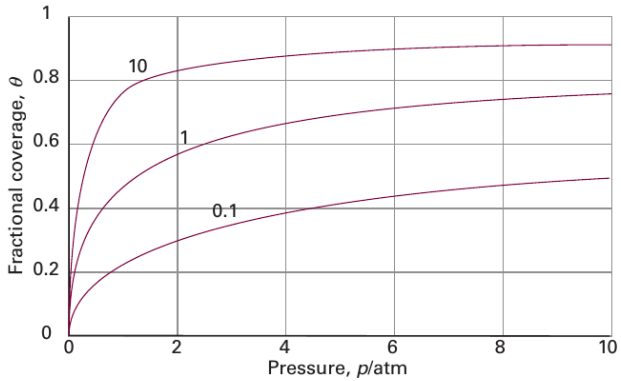

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$\Longrightarrow$ each surface atom hit once every $10^5 - 10^6$ or $\sim$once a day

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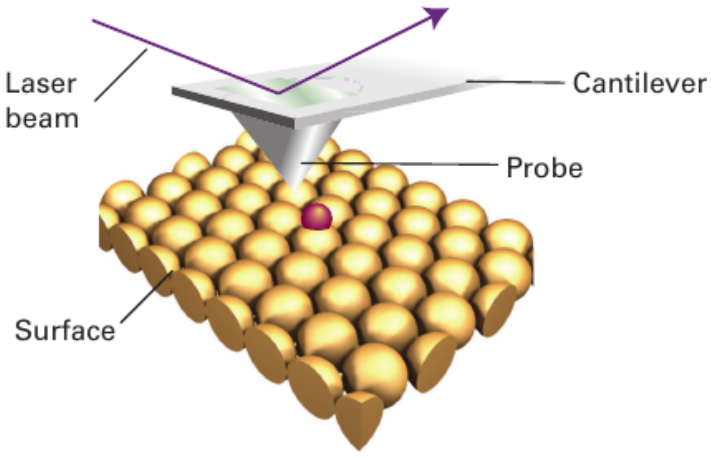
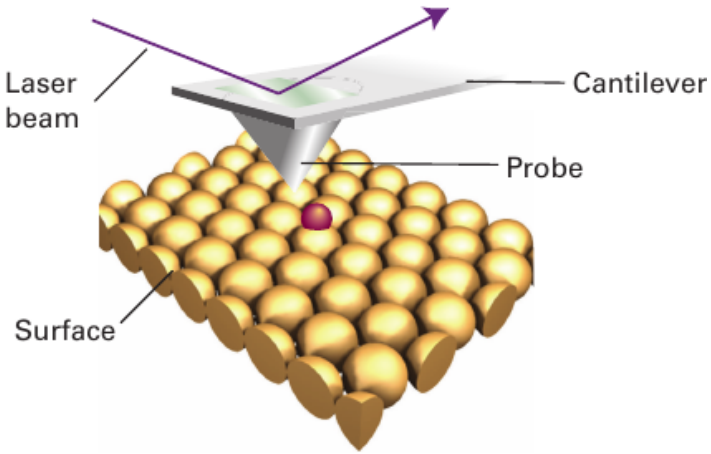


Atomic force microscopy (AFM)

sharpened tip attached to a cantilever is scanned across surface



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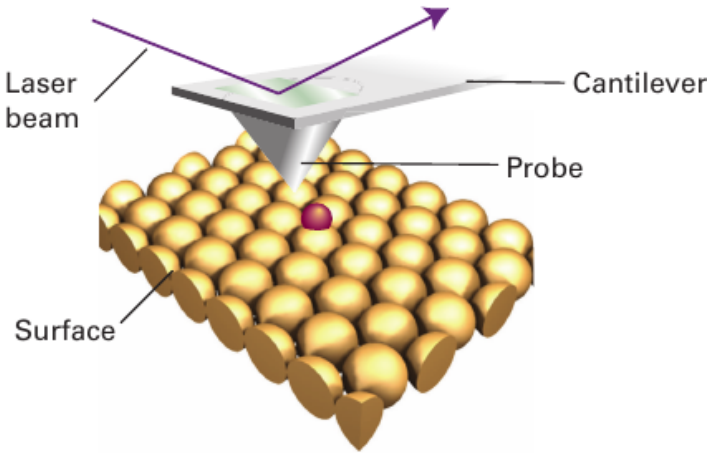

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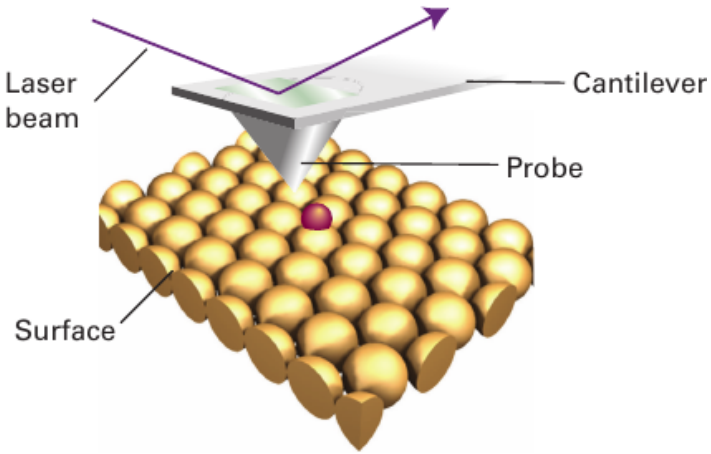

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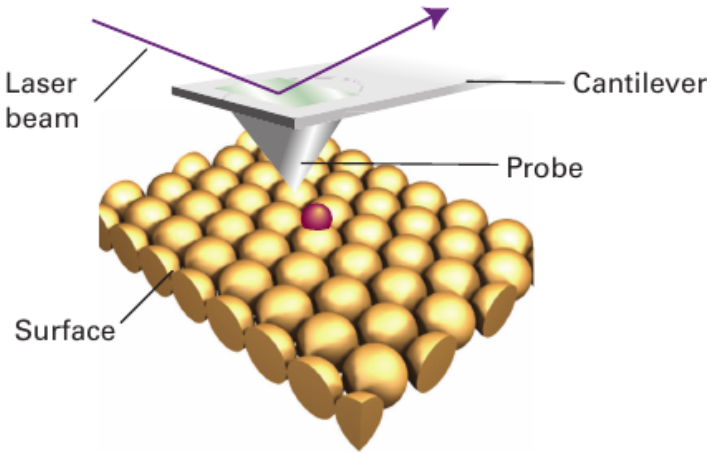

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$\therefore$ no current needs to pass between sample and probe, the technique can be applied to non-conducting surfaces and to liquid samples

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In ‘non-contact’, or ‘tapping mode’, the tip bounces up and down with specified frequency and never quite touches the surface
Amplitude of the tip’s oscillation changes when it passes over species adsorbed on surface

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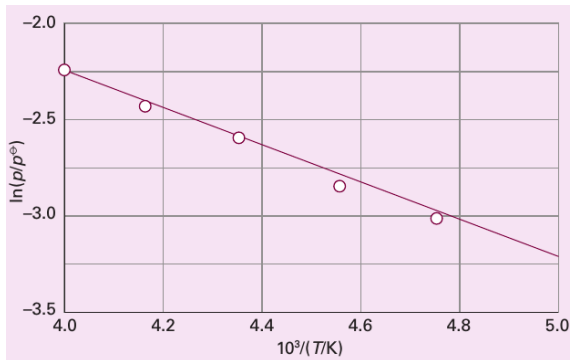

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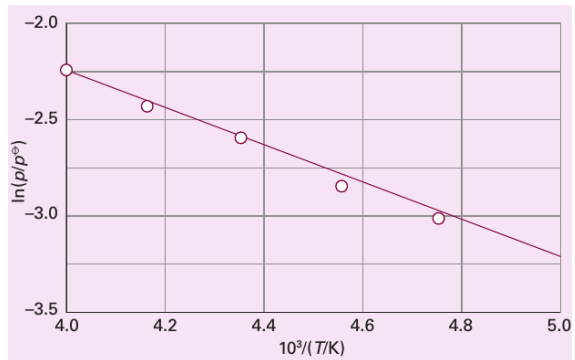

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• number of isotherms deal with cases where deviations from Langmuir isotherm are important

BET isotherm: accounts for multilayer adsorption

$\frac{V}{V_{mon}} = \frac{cz}{(1-z)\{1-(1-c)z\}}$ with $z = \frac{p}{p^*}$; $c = e^{\left(\Delta_{des}H^{\ominus} - \Delta_{vap}H^{\ominus}\right)}$

p^* =vapour pressure above a layer of adsorbate that is more than one molecule thick and which resembles pure bulk liquid

V_{mon} =volume corresponding to monolayer coverage

BET isotherm fits experimental observations moderately well over restricted pressure ranges,

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Freundlich isotherm : accounts for substrate–substrate interactions

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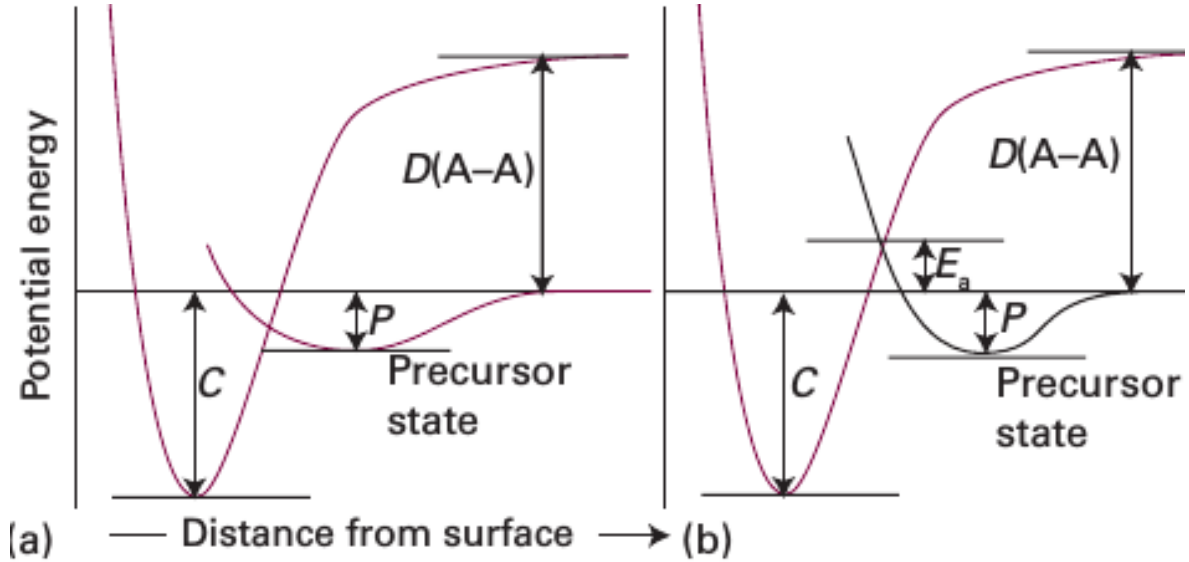

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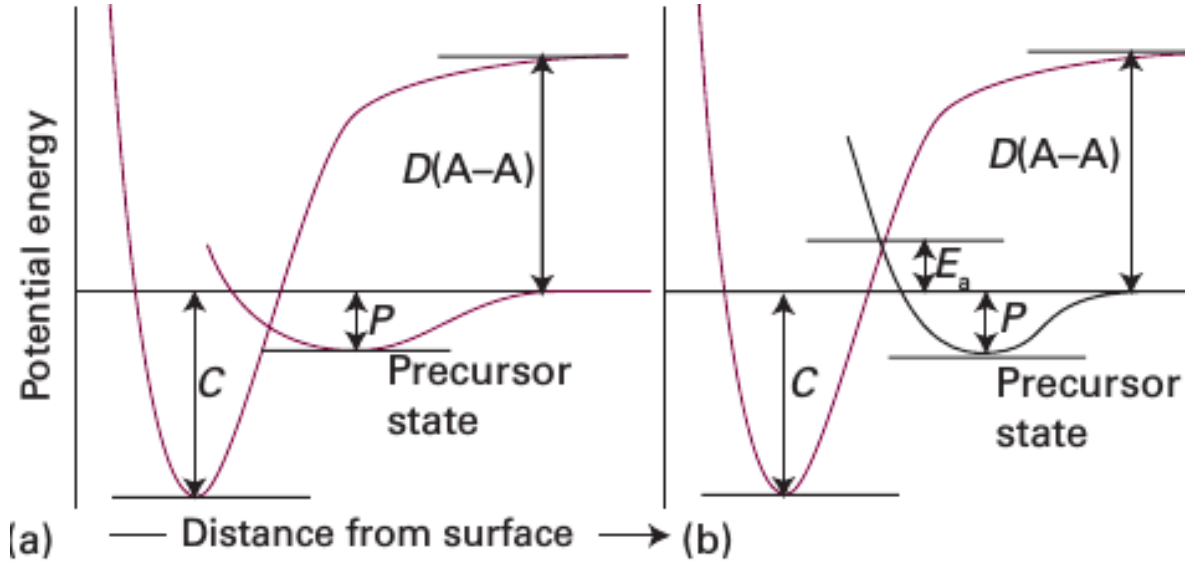

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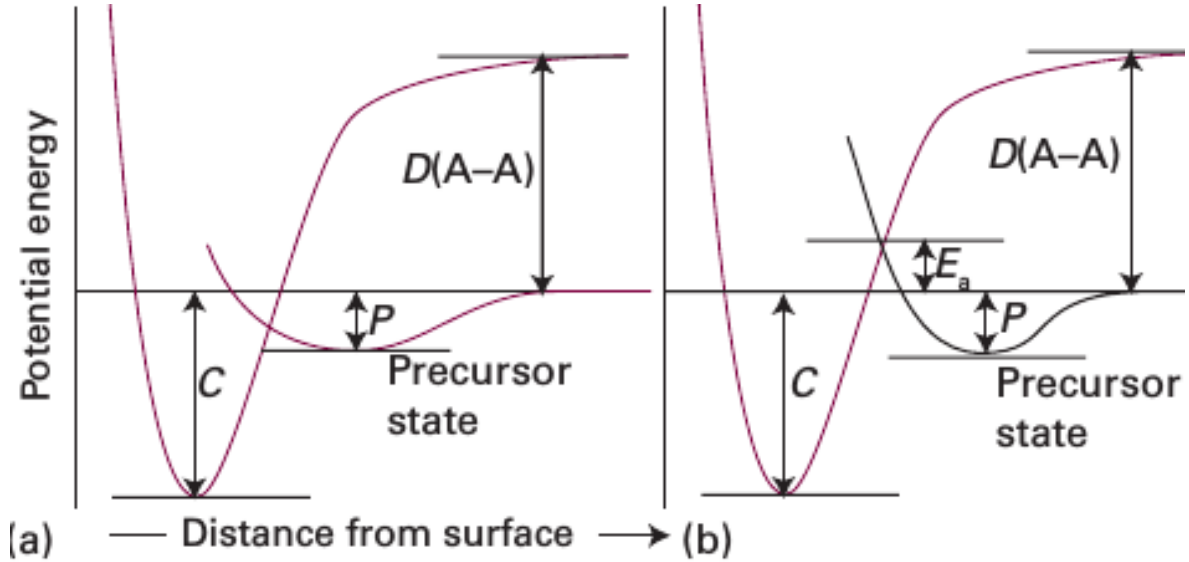

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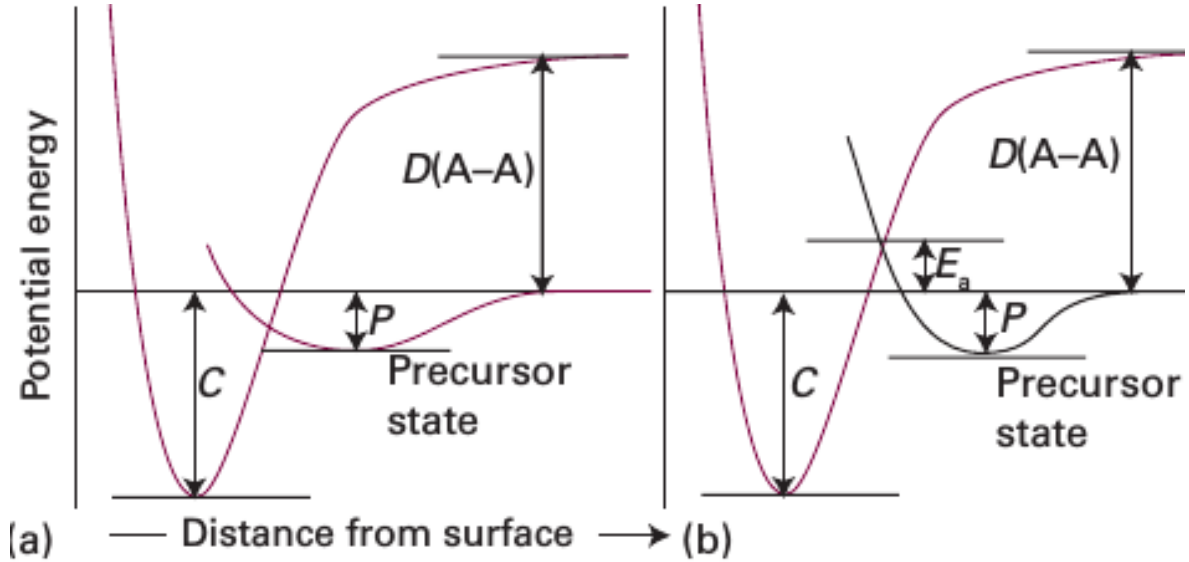

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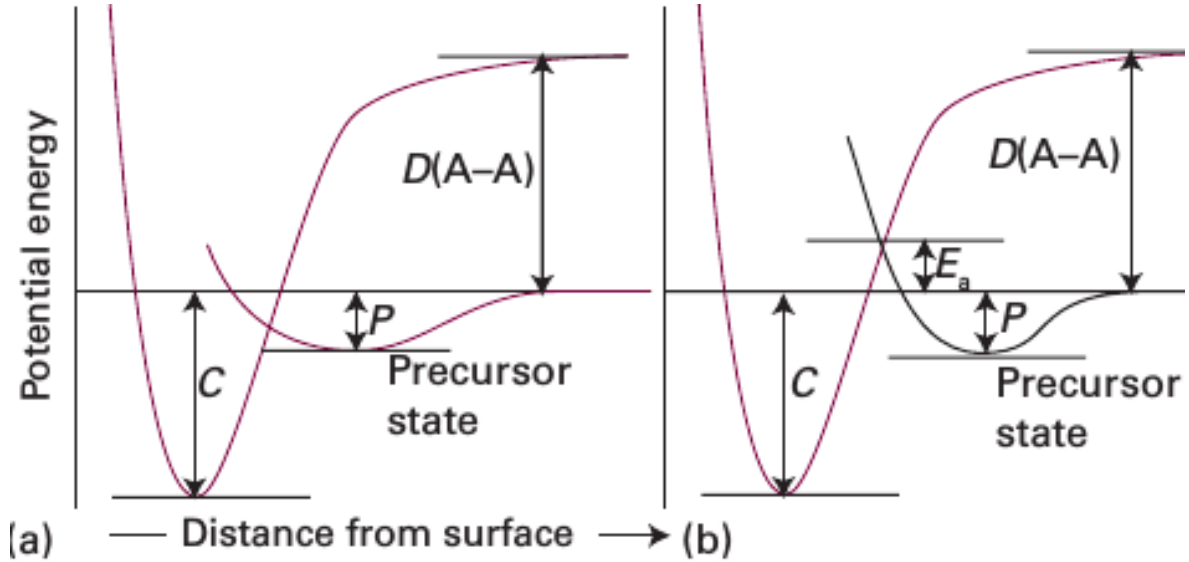

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Physisorption is usually fast, but can appear slow if adsn. takes place on porous medium

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I	28
II	33

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II	33

ratio of rates of chemisorption on equal areas of the two faces at 250 K is

$$\frac{\text{Rate}(1)}{\text{Rate}(2)} = \frac{Ae^{-\frac{E_{act}(1)}{RT}}}{Ae^{-\frac{E_{act}(2)}{RT}}} = 11$$

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but for N_2 on Rhenium, $s < 10^{-2}$

Simple assumption : $s = (1 - \theta)\, s_0$,

where s_0 =sticking probability on a perfectly clean surface

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Lifetimes close to 1 s are obtained by lowering T to ≈ 100K
For chemisorption, with $E_d \approx 100$kJ mol^{-1},and $\tau_0 = 10^{-14}$s,
we get residence half-lives$\approx$ 3000s at room temp and 1 s at 350 K