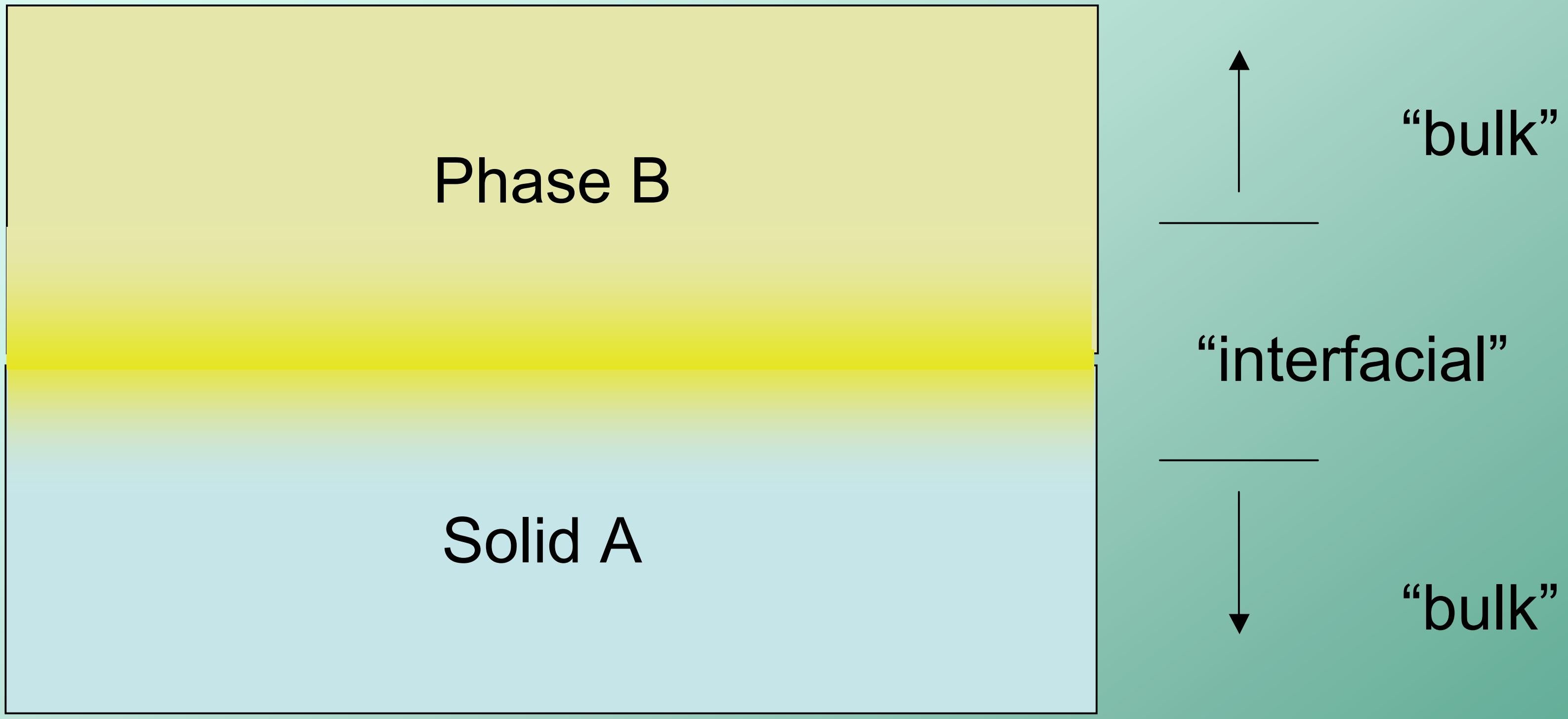
Solid surfaces



Phase B

“bulk”

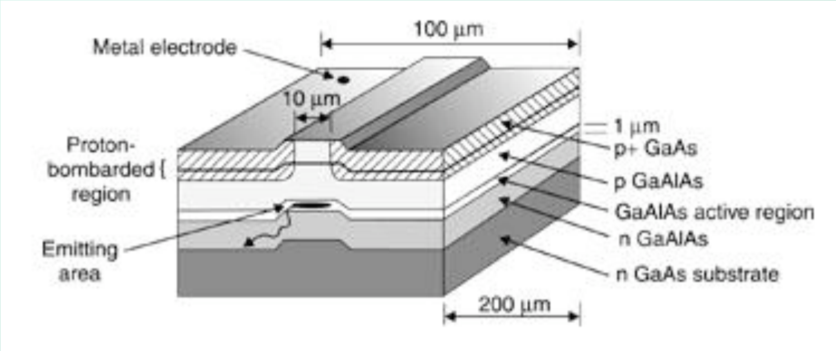
“interfacial”

Solid A

“bulk”

In the applications of chemistry we are frequently concerned with how a solid phase interacts with its environment

Solid -Solid



- *Adhesion and coatings*
- *Functional solid state devices*
- *Nanotechnology*

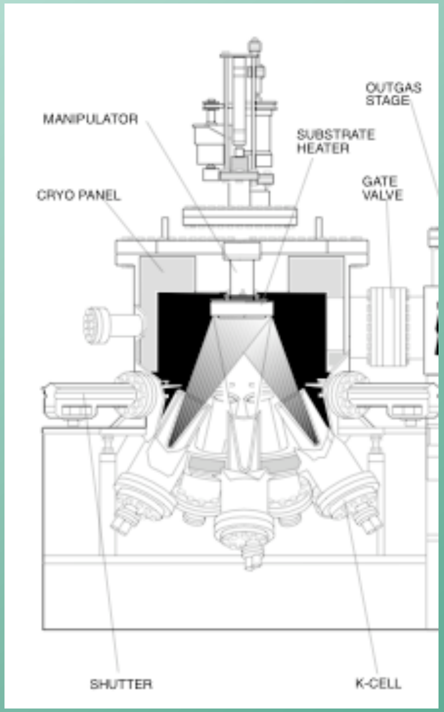
Solid liquid

- Electrochemistry
- Detergent action

Solid gas

- Catalysis

Thin films



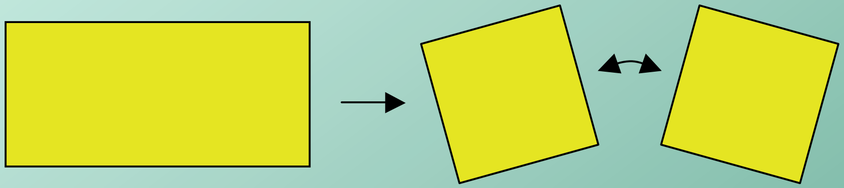
In this introduction we will focus on the chemistry of the gas-solid interface

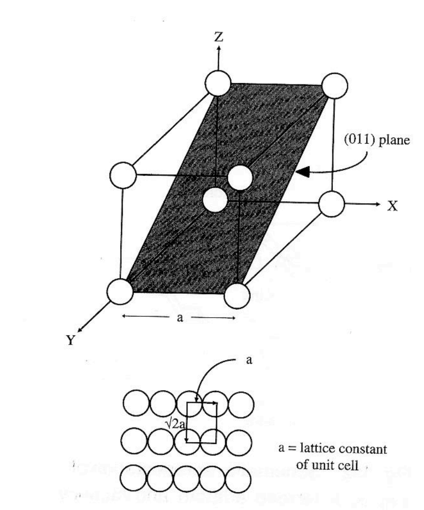
Books

- Atkins “Physical Chemistry”
- Attard “Surfaces” (Oxford chemistry primer)
- Bowker “Heterogeneous catalysis” (Oxford chemistry primer)
- Gasser “An Introduction to Chemisorption and Catalysis by Metals” (College libraries etc)

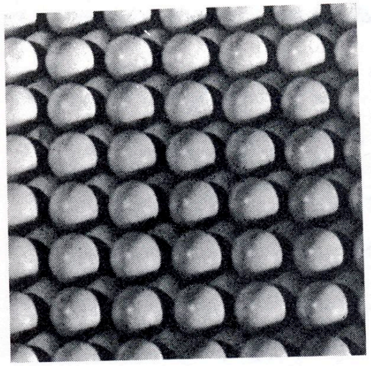
Atomic structure at solid surfaces

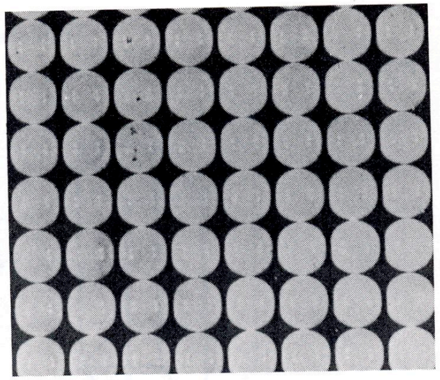
- Consider preparation of a surface by cleavage of a bulk single crystal
- Atomic structure will depend on how the surface is oriented w.r.t. the unit cell

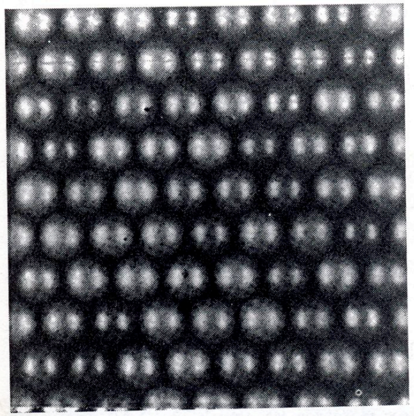


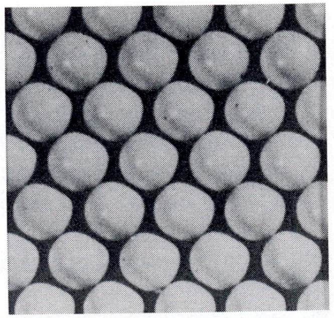


Surface lies parallel to a dense atomic plane in the bulk crystal


bcc (100)


fcc (100)


hcp (001)


bcc (110)

- Expect to see atomically ordered smooth surfaces

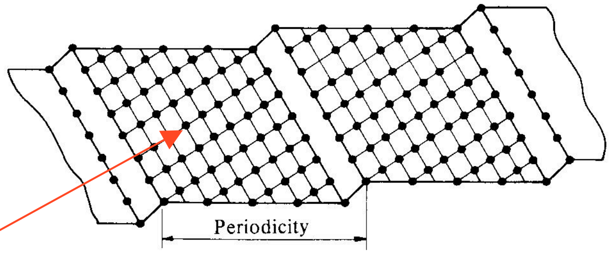
Surface is tilted w.r.t. to dense crystal planes

- Atomically rough
- TSK model - terrace-step-kink

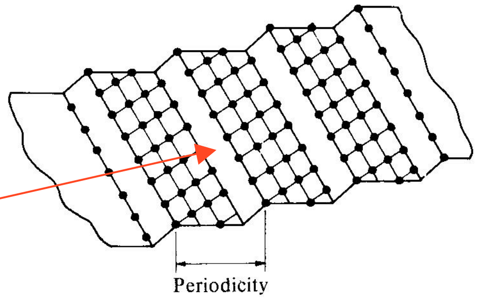
Terrace

Step

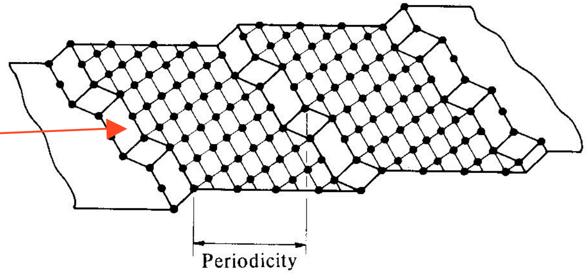
Kink



Stepped Pt (544) or Pt (S) [9(111) × (100)]

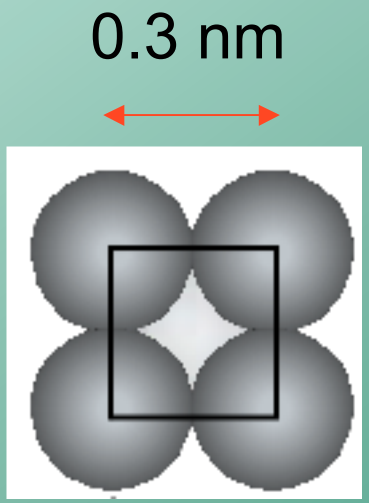


Stepped Pt (533) or Pt (S) [4(111) × (100)]



Kinked and stepped Pt (679) or Pt (S) [7(111) × (310)]

Atomic concentration



- Area of unit cell $=(0.3 \times 10^{-9})^2$ m^2
- 1 atom per unit cell
- Therefore $1/\ (0.3 \times 10^{-9})^2$

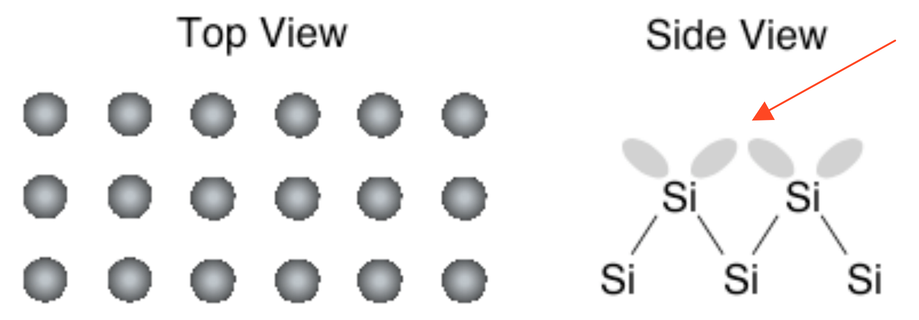
$= 1.1 \times 10^{19}$ atoms m^{-2}

$= 1.1 \times 10^{15}$ atoms cm^{-2}

Order of magnitude correct for most surfaces

Chemical reactivity of surfaces

- Clean surfaces are often highly reactive -"unsatisfied valence"



Dangling bonds

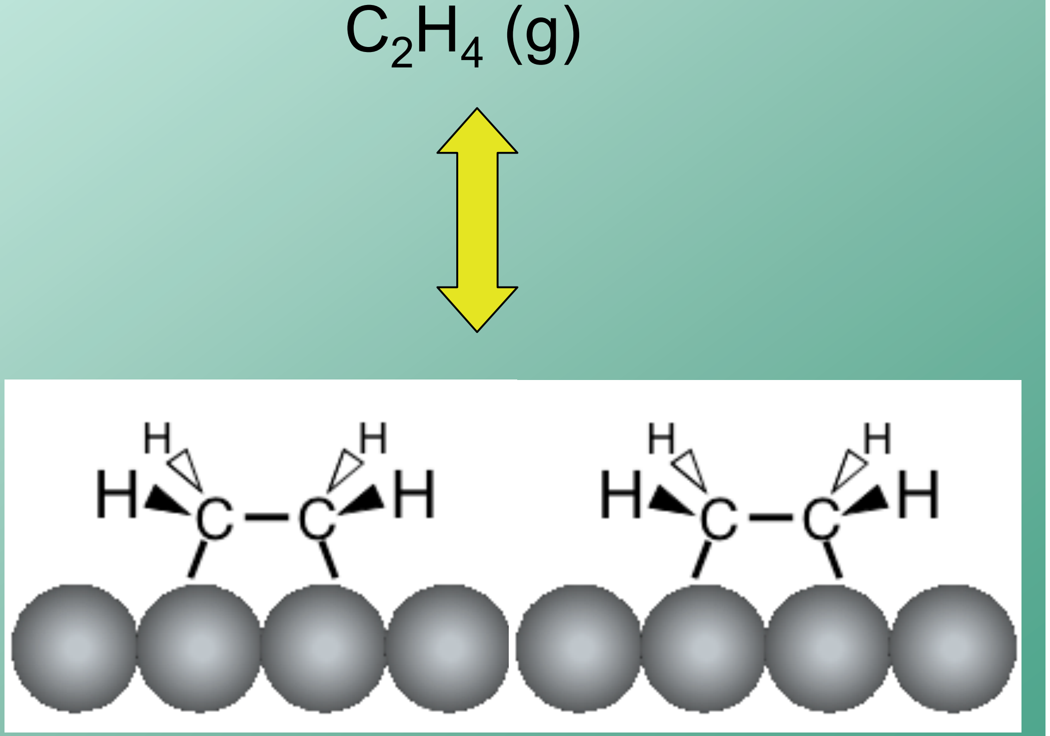
Surface - 2 coord.

Bulk - 4 coord

- Therefore expect to react with ambient gaseous species

Adsorption

- Gaseous molecule becomes trapped at the surface and forms a bond to it.
- Don’t confuse it with absorption!



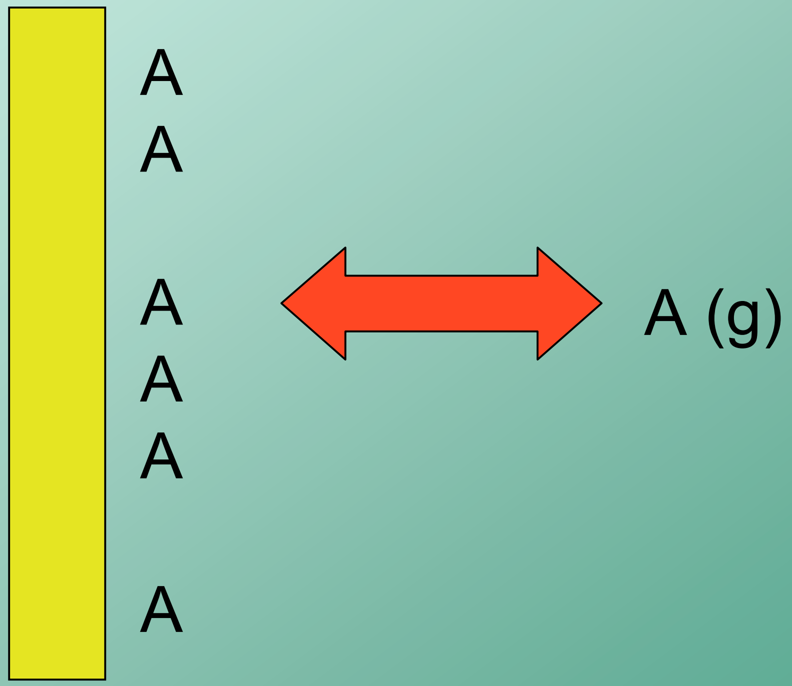
Silver Surface

Thermodynamics

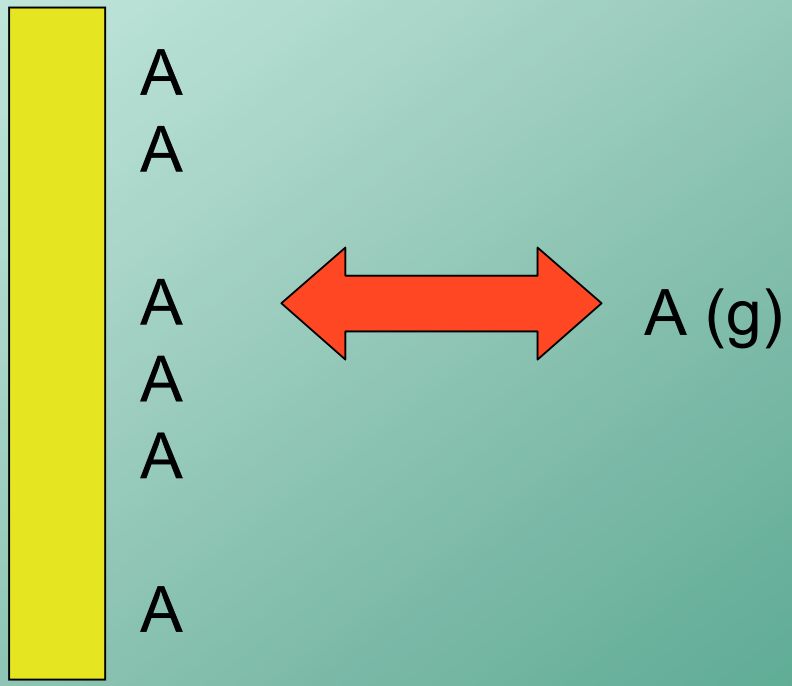
- ΔS_{ads} = entropy of (adsorbed phase -gas phase)
- ΔH_{ads} = enthalpy of (adsorbed phase-gas phase)
- ΔS_{ads} is negative (loss of disorder)
- However so is ΔH_{ads}(exothermic process)
- So occurs spontaneously (exoergic process driven by the enthalpy of bond formation)

Adsorption Isotherms

- Consider equilibrium between adsorbed and gas phase
- Extent of adsorption will increase as i. P_A rises; ii. T falls (Le Chatelier etc.)



- θ_A = fraction of surface occupied with adsorbed A.
- Then expect $\theta_A = f(P_A, T)$
- At a constant temperature $\theta_A = f(P_A)$
- *This relationship is known as the adsorption* isotherm



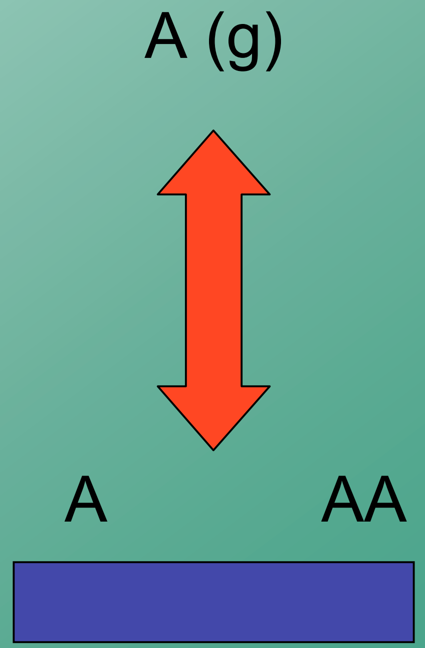
Langmuir adsorption isotherm

- Recap 2nd yr

$$\begin{aligned} &\textit{adsorption rate} \propto \textit{pressure} \times \textit{conc. of bare surface} \\ &\qquad = k^{ads}\left(1-\theta_A\right)p_A \end{aligned}$$

$$\begin{aligned} &\textit{desorption rate} \propto \textit{conc. of adsorbate} \\ &\qquad = k^{des}\theta_A \end{aligned}$$

$$\boxed{\theta_A = \frac{Bp_A}{1+Bp_A} \quad \text{where} \quad B = \frac{k^{ads}}{k^{des}}}$$

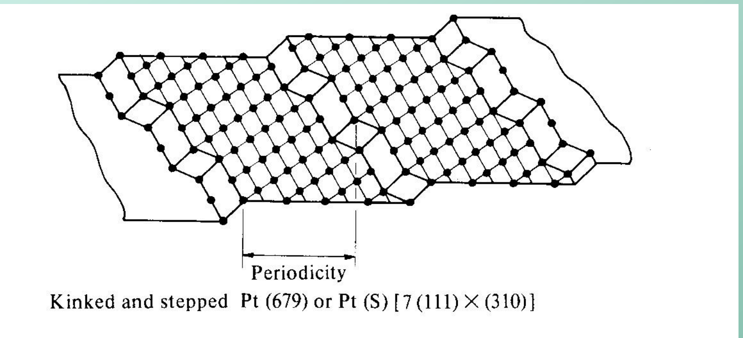


But…..

- Isotherm is an equilibrium property - normally understood by considering state of reactants and products.
- Above derivation does’nt identify what adsorbed phases it might apply to (all?)
- Experimental measurement of the kinetics of adsorption/desorption shows the assumptions above seldom apply!

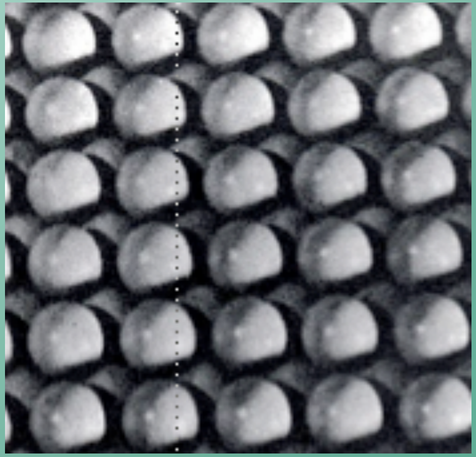
Langmuir isotherm using a statistical mechanics approach

- Surface is a uniform array of adsorption sites



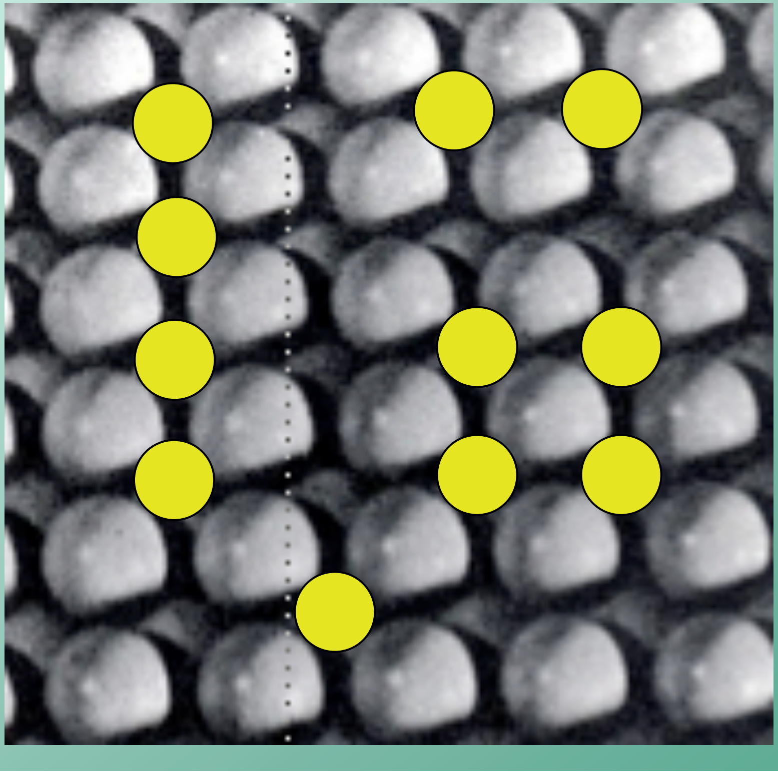
Kinked and stepped Pt (679) or Pt (S) [7 (111) × (310)]

✗



✓

- Adsorbed phase consists of species localised in a fraction θ of the available sites.
- No interaction between species on adjacent sites (i.e. random occupancy)



The configurational entropy of the adsorbed phase

- A normal "distinguishable system" with some extra configurational entropy.

A		A	A		A	A	

- *M* sites (boxes), N molecules. θ = *N/M*

$$S^{config} = k \ln W^{config} = k \ln\left(\frac{M.(M-1)(M-2)....}{N!} \right)$$

$$= k \ln\left(\frac{M!}{(M-N)!N!} \right)$$

The Helmholtz energy of the adsorbed phase

$$A^{normal} = U - TS = N\varepsilon_o - NkT\ln q$$

$$A^{ads} = N\varepsilon_o - NkT\ln q - TS^{config}$$

$$= N\varepsilon_o - NkT\ln q - kT\ln\left(\frac{M!}{(M-N)!N!}\right)$$

Equation 1

Use of Stirling approx. (lnx!=xlnx-x) (optional)

Equation 2

$$\ln\left(\frac{M!}{(M-N)!N!}\right)$$

$$= k\left[M\ln M - N\ln N - (M-N)\ln(M-N)\right]$$

- Inserting (2) into (1) yields *A* for the adsorbed phase, and differentiating with respect to *N* yields the chemical potential of this phase since from stat mechs

$$\mu = \left(\partial A \middle/ \partial N\right)_T$$

The result for the chemical potential (optional)

$$\mu^{ads} = \varepsilon_o^{ads} - kT\ln q^{ads} - kT\ln\left((M-N) \big/ N \right)$$

$$= \varepsilon_o^{ads} - kT\ln\left[q^{ads}\left(1/\theta - 1 \right) \right]$$

$$\mu^{gas} = \varepsilon_o^{gas} - kT\ln\left[\frac{\left(q_{gas}/V \right) kT}{p_{gas}} \right]$$

The isotherm!

- At equilibrium $\mu^{gas} = \mu^{ads}$ which yields after rearrangement

$$\theta_A = \frac{Bp_A}{1 + Bp_A}$$

"Langmuir isotherm"

$$B = {}^{1}\!/_{kT}\left({q^{ads}} \Big/ \left({q^{gas}} / {V} \right) \right) \exp\left({\varepsilon_o^{gas} - \varepsilon_o^{ads}} \Big/ {kT} \right)$$