Recall

Overall objective: **understanding interfacial structure at metal|solution interface**

Considered several models – assumptions:

- **Ideal metal surface, no explicit electronic structure taken into account, uniformly distributed surface charge density, σ^M, controlled by E**

- **Ions in solution: characterized by magnitude of charges and possibly their radii (Stern, Grahame models), solvation shells, partial or complete desolvation, besides that: ignore their chemical identities**

  $\Rightarrow$ **Non-specifically adsorbed**

$\Rightarrow$ **So far, only long-range electrostatic effects as origin for charge accumulation/depletion in space charge region**

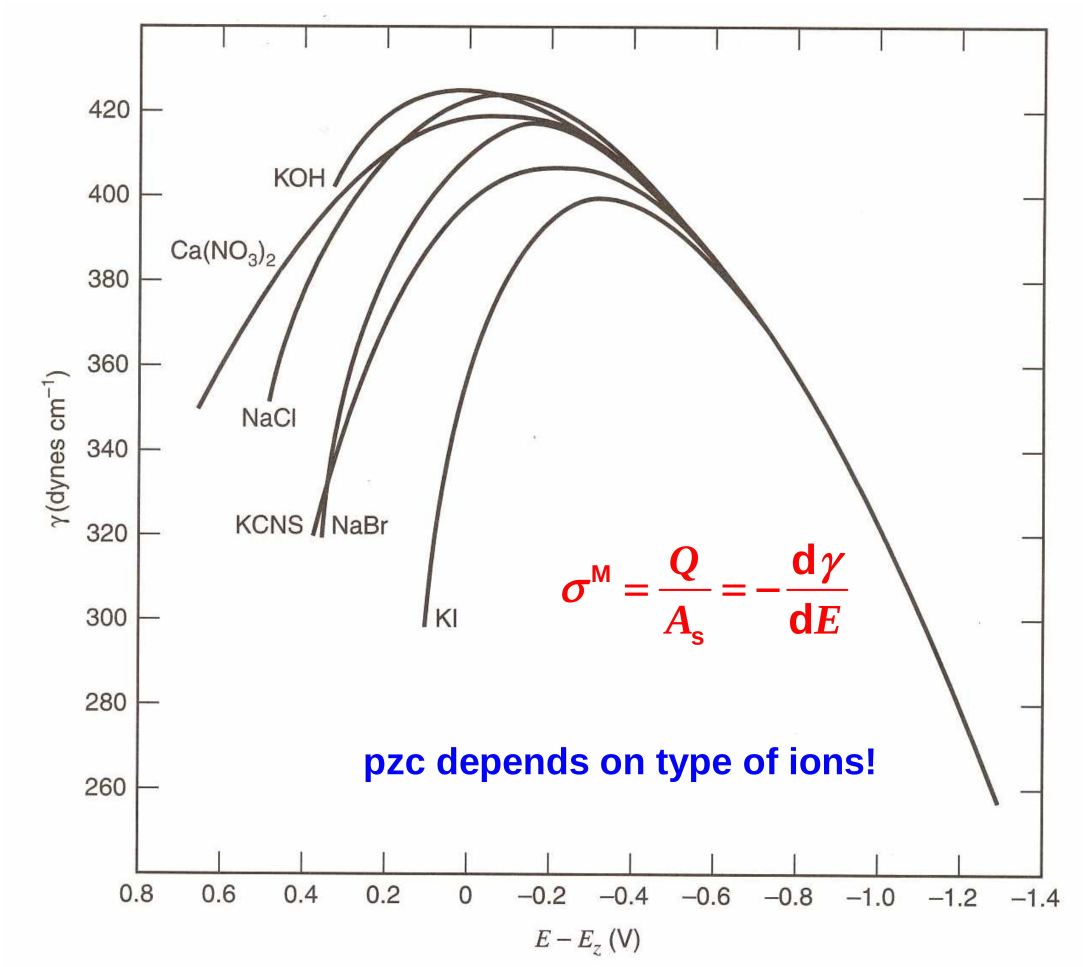
Experimental observation:

more positive $E > E_z$ (favoring accumulation of anions)

$\Rightarrow$ chemical identity of ions becomes important!

Example:

Electrocapillary curves of surface tension vs *E* for Hg in contact with solutions of indicated electrolytes at 18℃ [from D.C. Grahame, Chem. Rev. 41, 441, 1947.]



$$\sigma^{M} = \frac{Q}{A_s} = -\frac{d\gamma}{dE}$$

pzc depends on type of ions!

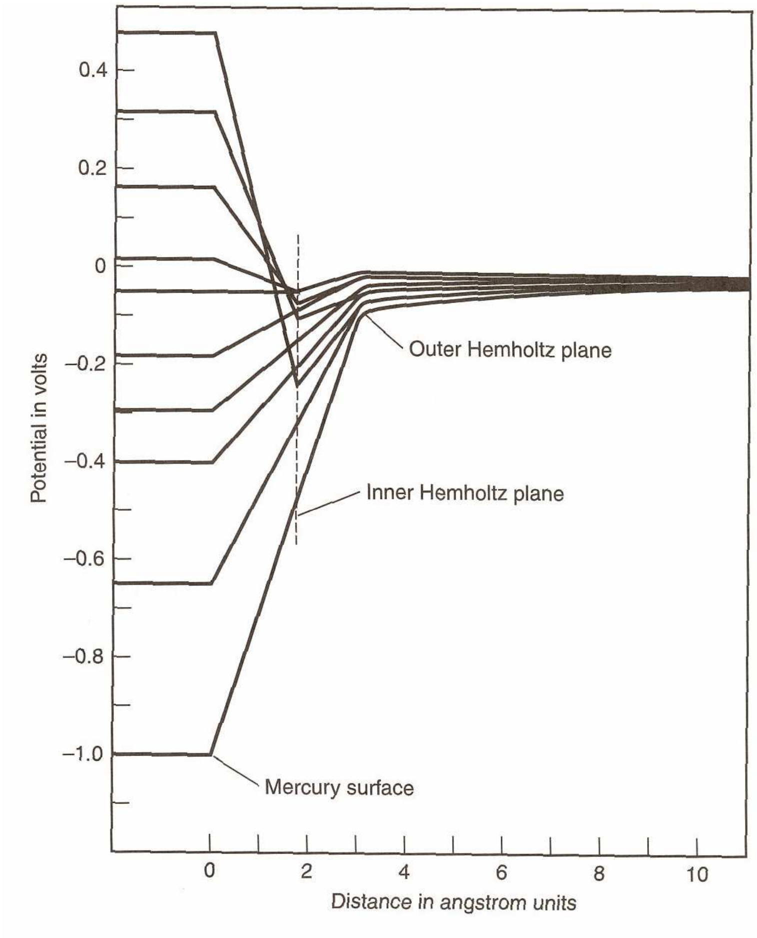
“Negative” potentials, $E < E_z$: surface tension on Hg independent of composition of the electrolyte – results in line with Gouy-Chapman and Stern models

□ no specific adsorption.

“Positive” potentials, $E > E_z$: major effect due to anion excess □ specific adsorption of anions on Hg, strong chemical interactions

Potential profiles in interfacial zone in presence of specific adsorption for Hg in contact with NaCl (Cl^-, Br^-, I^- specifically adsorb on Hg, F^- does not)

[from D.C. Grahame, Chem. Rev. 41, 441, 1947.]



Specific adsorption of anions at positive potentials induces an excess of cations in the diffuse layer!

What happens upon increasing the electrolyte concentration?

- **More adsorption □ shift to more negative φ at IHP!**
- **PZC shifts to more negative values**

Specific Adsorption on Metal Electrodes

Concentration of species at interface larger than accounted for by electrostatic interactions

☐ specific adsorption

Most important quantity: binding or adsorption energy

- **Chemical interactions (adsorbate – electrode)**
  - **☐ chemisorption → binding energies > 0.5 eV**
- **Weaker physical interactions**
  - **☐ physisorption → binding energies < 0.5 eV**

Adsorption involves partial desolvation

Cations (smaller radius)

☐ firmer solvation sheath than anions

☐ less likely to be adsorbed

Amount of adsorbed species: coverage θ – fraction of surface sites (adsorption sites) covered with adsorbate

☐ $$\theta = \frac{\text{number of adsorbed species}}{\text{number of surface atoms of the substrate}}$$

Most electrochemical studies: utilize well-defined single-crystal solid surfaces of metals or semiconductors

Chemisorption: distinct positions possible – depending on crystallographic structure of the surface

Experimental probes of adsorption phenomena:

- **Electrochemical methods:**
  - **electrocapillarity**
  - **cyclic voltammetry**
  - **transient measurements (chronoamperometry, e.g. CO monolayer oxidation)**
- **Spectroscopic and microscopic methods:**
  - **surface enhanced Raman spectroscopy SERS**
  - **IR spectroscopy**
  - **scanning tunneling microscopy**

Study specific adsorption of particular ionic species: add excess (high concentration) of inert, non-adsorbing electrolyte → supporting electrolyte

Why supporting electrolyte?

No interference of adsorption phenomena with double layer charging effects (problem sets).

Adsorption isotherms

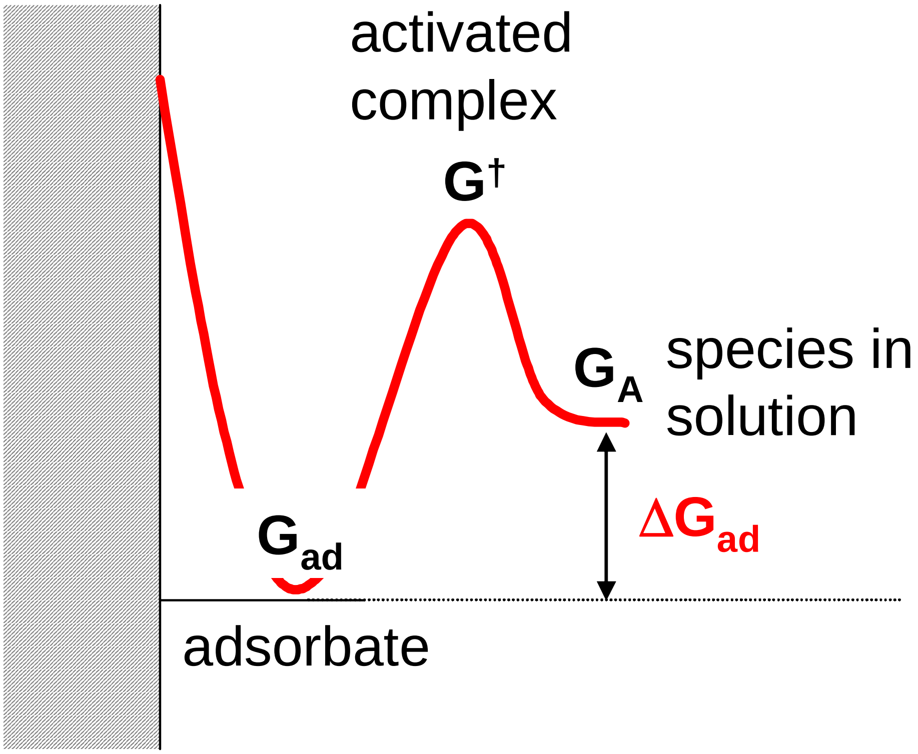
How does coverage of a species A on electrode surface vary with concentration c_A in bulk solution (all other variables fixed, in particular temperature)?

Adsorption: stochastic process between free surface sites on electrode and species A in solution.

What are the rates/probabilities of elementary reaction events, i.e. adsorption and desorption?

Need a theory of the kinetics of individual processes – not limited to thermodynamic equilibrium states!

Use absolute rate theory (a.k.a. transition state theory or activated complex theory): adsorption/desorption are activated processes – overcome potential energy barrier



Principle:

borrow potential energy from kinetic energy of environmental degrees of freedom

$$\Delta G_{ad} = G_{ad} - G_A$$

Rate of adsorption proportional to

- **Probability of $(1-\theta)$ finding free surface site**
- **Probability of having species A near surface, c_A**
- **Probability of overcoming activation barrier**

$$v_{ad} = K_{ad} c_A (1-\theta) \exp\left(-\frac{G^{\dagger} - G_A}{RT}\right)$$

$G^{\dagger}$ **molar Gibbs free energy of the activated complex**

G_A **molar Gibbs free energy of A in solution**

Similar: rate of desorption

$$v_{\mathrm{des}} = K_{\mathrm{des}} \theta \exp\left(-\frac{G^{\dagger} - G_{\mathrm{ad}}}{RT}\right)$$

G_{ad} molar Gibbs free energy of the adsorbate

K_{ad}, K_{des} are constants (statistical mechanics, quantum theory). They determine the time scale of both processes.

At (dynamic) equilibrium:

$$\frac{\mathrm{d}\theta}{\mathrm{d}t} = v_{\mathrm{ad}} - v_{\mathrm{des}} = 0$$

$$v_{\mathrm{ad}} = v_{\mathrm{des}} \Rightarrow \frac{\theta}{1-\theta} = \frac{K_{\mathrm{ad}}}{K_{\mathrm{des}}} c_{\mathrm{A}} \exp\left(-\frac{\Delta G_{\mathrm{ad}}}{RT}\right)$$

adsorption isotherm

ΔG_{ad} molar Gibbs free energy of adsorption:

$$\Delta G_{\mathrm{ad}} = G_{\mathrm{ad}} - G_{\mathrm{A}}$$

Several cases:

- ΔG_{ad} is independent of θ, i.e. no surface heterogeneities, no effective interactions between adsorbate molecules

  □ **Langmuir isotherm**

- effective interactions (mean field)

  □**Frumkin isotherm**

$$\Delta G_{\mathrm{ad}} = \Delta G^{0}_{\mathrm{ad}} + \gamma\theta \quad □$$

$$\boxed{\frac{\theta}{1-\theta} = \frac{K_{\mathrm{ad}}}{K_{\mathrm{des}}} c_{\mathrm{A}} \exp\left(-\frac{\Delta G^{0}_{\mathrm{ad}}}{RT}\right) \exp\left(-g\theta\right)}$$

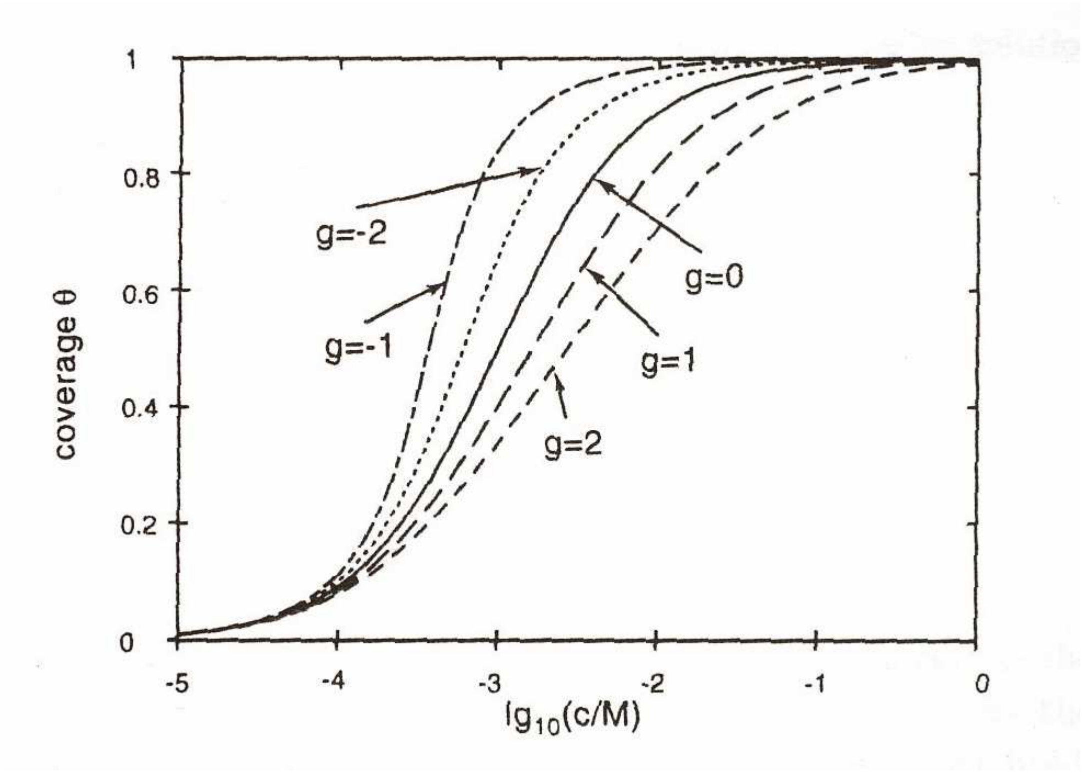
where $g = \dfrac{\gamma}{RT}$ is the Frumkin interaction factor:

repulsion: $g > 0$

attraction: $g < 0$

origin of g : surface heterogeneity,
adsorbate interactions

Frumkin isotherms for various values of g



Dependence on potential:

ΔG_{ad} depends on potential, different dependence for anions, cations and neutral species

Consider adsorption and discharge according to

$$A^{z+} + ze^{-} \leftrightarrow A_{\mathrm{ad}}$$

Langmuir isotherm with potential dependence of molar Gibbs free energy of adsorption

$$\Delta G_{\mathrm{ad}} = \Delta G_{\mathrm{ad}}^{0} + zF\left(\varphi - \varphi_{0}\right)$$

Resulting isotherm:

$$\frac{\theta}{1-\theta} = c_{\mathrm{A}} K \exp\left(-\frac{zF\left(\varphi-\varphi_0\right)}{RT}\right)$$ where $K = \frac{K_{\mathrm{ad}}}{K_{\mathrm{des}}} \exp\left(-\frac{\Delta G^0_{\mathrm{ad}}}{RT}\right)$

Simple adsorption isotherm (ideal reference case).

Study potential dependence of adsorption reaction: potential sweep

- **Start in region with negligible θ**
- **vary potential slowly with constant sweep rate**

$$v_{\mathrm{s}} = \frac{\mathrm{d}\varphi}{\mathrm{d}t}$$

  small enough: quasi-equilibrium, no DL charging

  large enough: sizable current

  practice: ~ few mV s^{-1}

- **measure resulting current.**

Resulting current (with above isotherm):

$$I = Q_0 \frac{\mathrm{d}\theta}{\mathrm{d}t} = Q_0 v_{\mathrm{s}} \left(-\frac{zF}{RT}\right) \theta\left(1-\theta\right)$$ **symmetry!**

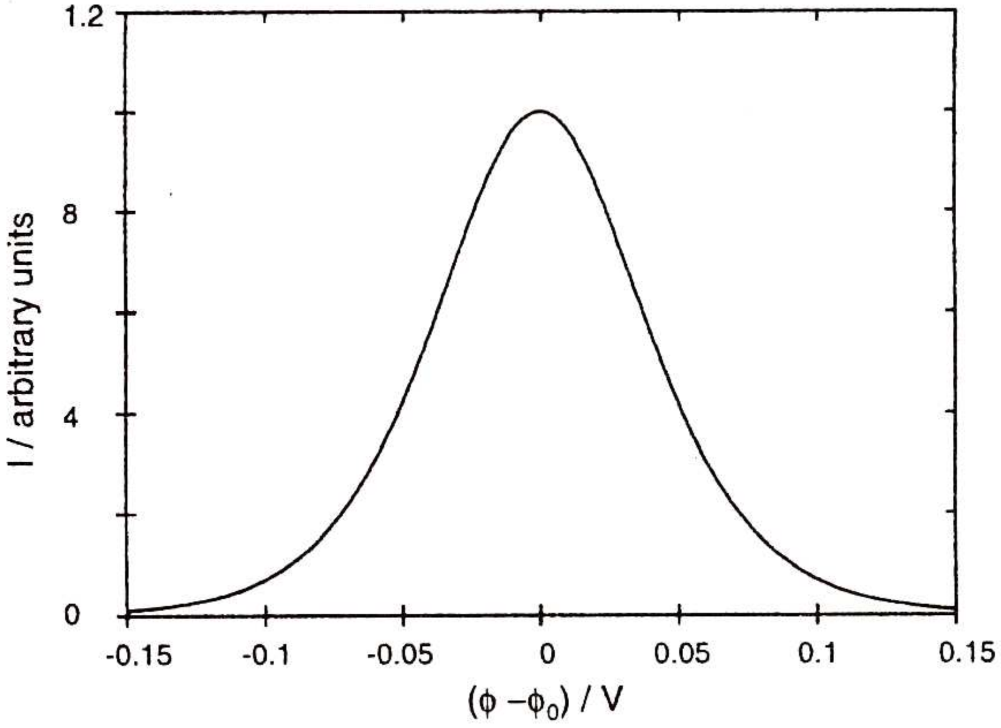
Q_0: charge for adsorption of one monolayer

Maximum current found at $\theta = 1/2$

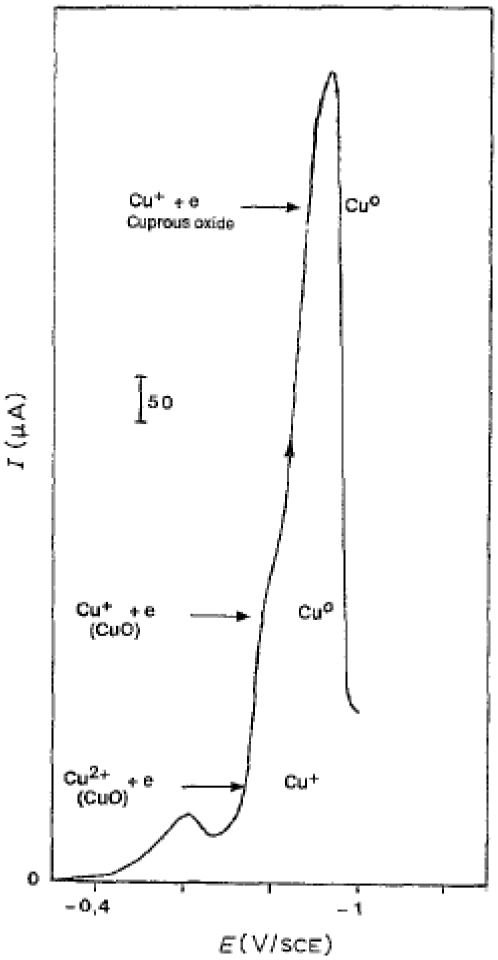
Coverage as a function of potential:

$$\theta(\varphi) = \frac{Q(\varphi)}{Q_0} = \frac{1}{Q_0}\int_{\varphi_1}^{\varphi} \frac{I}{v_s}\mathrm{d}\varphi$$

(φ_1: in region where no adsorption occurs)



Linear sweep voltammetry of copper oxidation



Identification of different species present

in corrosion layers of copper surface

The structure of single crystal surfaces

Most solids: not crystalline on their surface (restructuring, amorphous, oxidized).

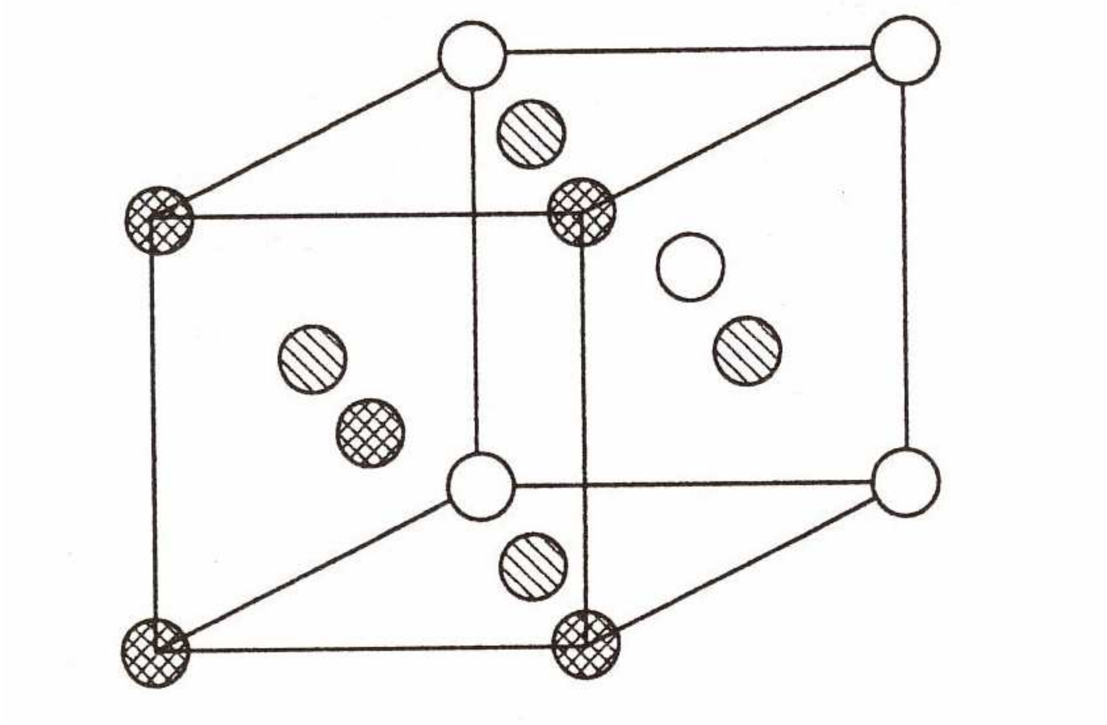
Is it academic to study crystalline surfaces? – No!

- **Well-defined structure → reproducibility**
- **Periodicity → facilitates theoretical description, diffraction methods**
- **Semiconductor industry**

Important metals in electrochemistry (Au, Ag, Cu, Pt, Pd, Ir):

fcc structure (face centered cubic)

Conventional unit cell: fcc lattice with lattice constant a

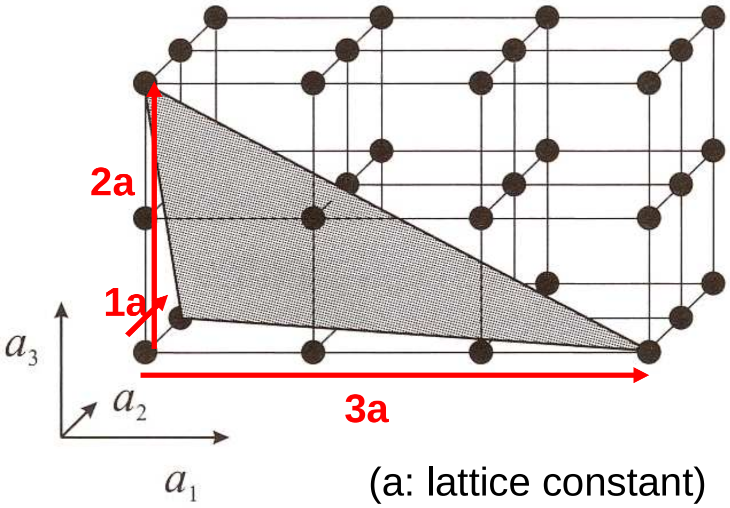


Surface structure

(cutting plane through certain points of unit cell)

□ bulk crystal structure + orientation of cutting plane

Particular surface plane: defined through components of normal vector to that plane, the so-called Miller indices

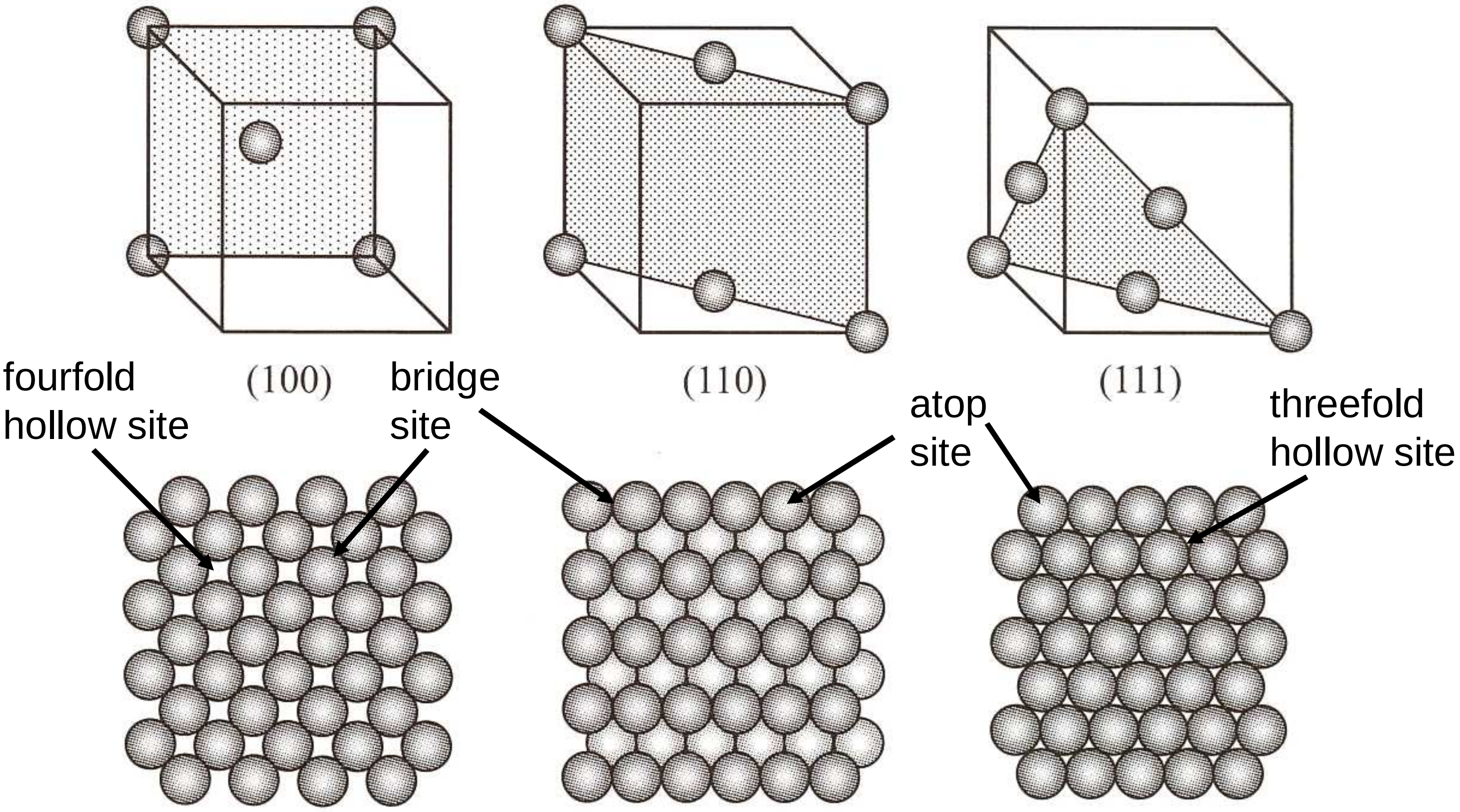


(a: lattice constant)

How are they determined?

- **Find intersection of cutting plane with crystal axes,**
  e.g. (for the simple cubic lattice above) the components are 3,1,2
- **Take inverse of these values,**
  e.g. 1/3, 1/1, 1/2
- **Use smallest possible multiplicator,**
  e.g. 6 □ Miller indices (263)

Important surface planes of fcc lattice



Distinct crystal surfaces: **particular sites for adsorption.**

Densities of surface sites:

e.g. Pt, lattice constant a = 3.9 Å

Pt(100): surface atom density $\frac{2}{a^2} = 1.3 \cdot 10^{15}\ \text{cm}^{-2}$

Pt(110): $\frac{\sqrt{2}}{a^2} = 0.93 \cdot 10^{15}\ \text{cm}^{-2}$

Pt(111): $\frac{4}{\sqrt{3}a^2} = 1.5 \cdot 10^{15}\ \text{cm}^{-2}$