



Chemical Kinetics and Reaction Dynamics

Part III Solids and Surface Chemistry



Further reading/references:

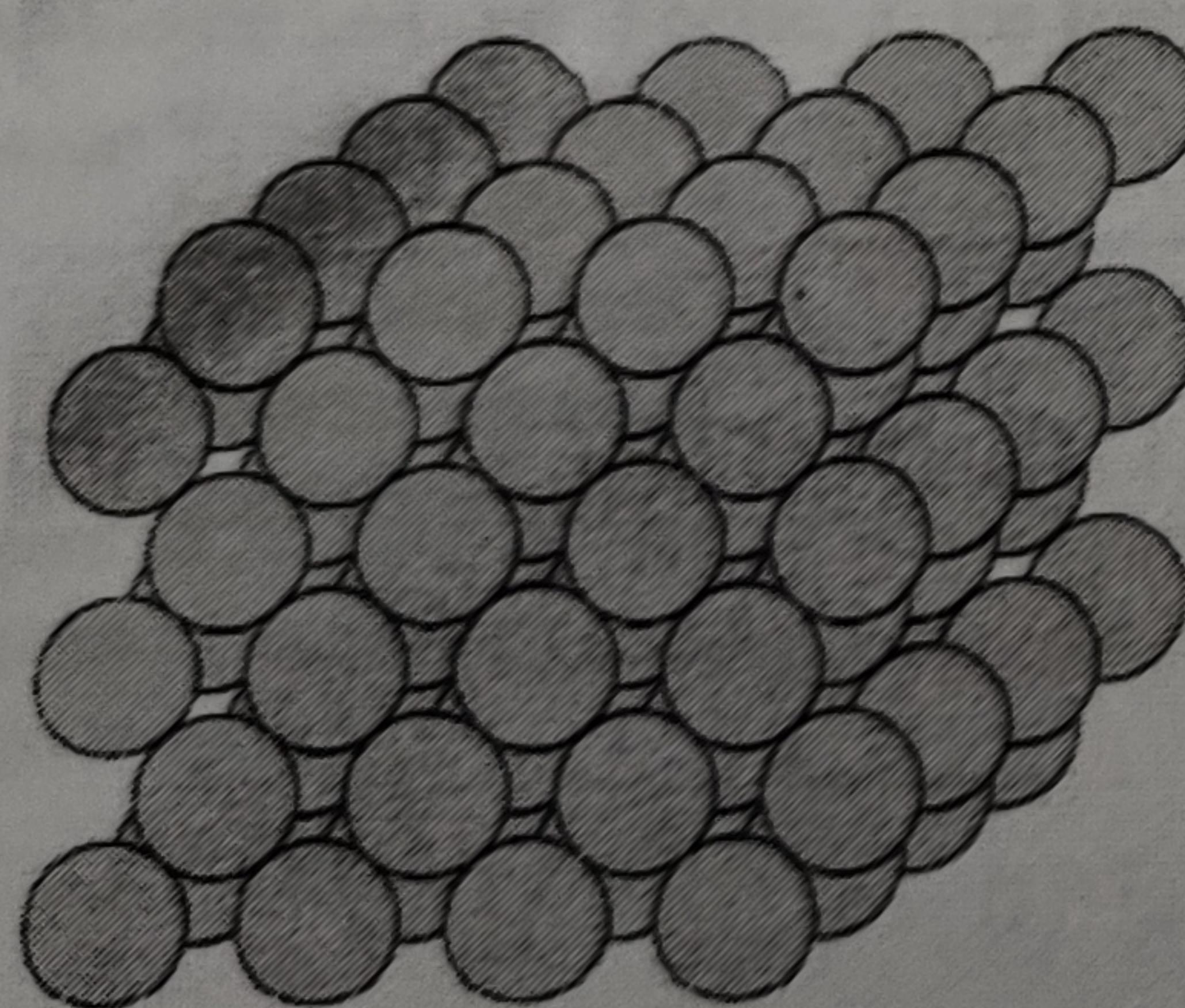
- D. A. McQuarrie, J. D. Simon, *Physical Chemistry: A Molecular Approach*, pp. 1271-1311, (University Science Books, 1997).
- E. Zolotoyabko, *Basic Concept of Crystallography*, pp. 1-32, (Wiley-VCH Boschstr, 2011).
- P. L. Houston, *Chemical Kinetics and Reaction Dynamics*, pp. 171-203, (Dover Publications, Inc., New York, 2006).

1

2



1. The Unit Cell Is the Fundamental Building Block of a Crystal



copper atoms in a copper crystal

the crystal possesses a periodic structure

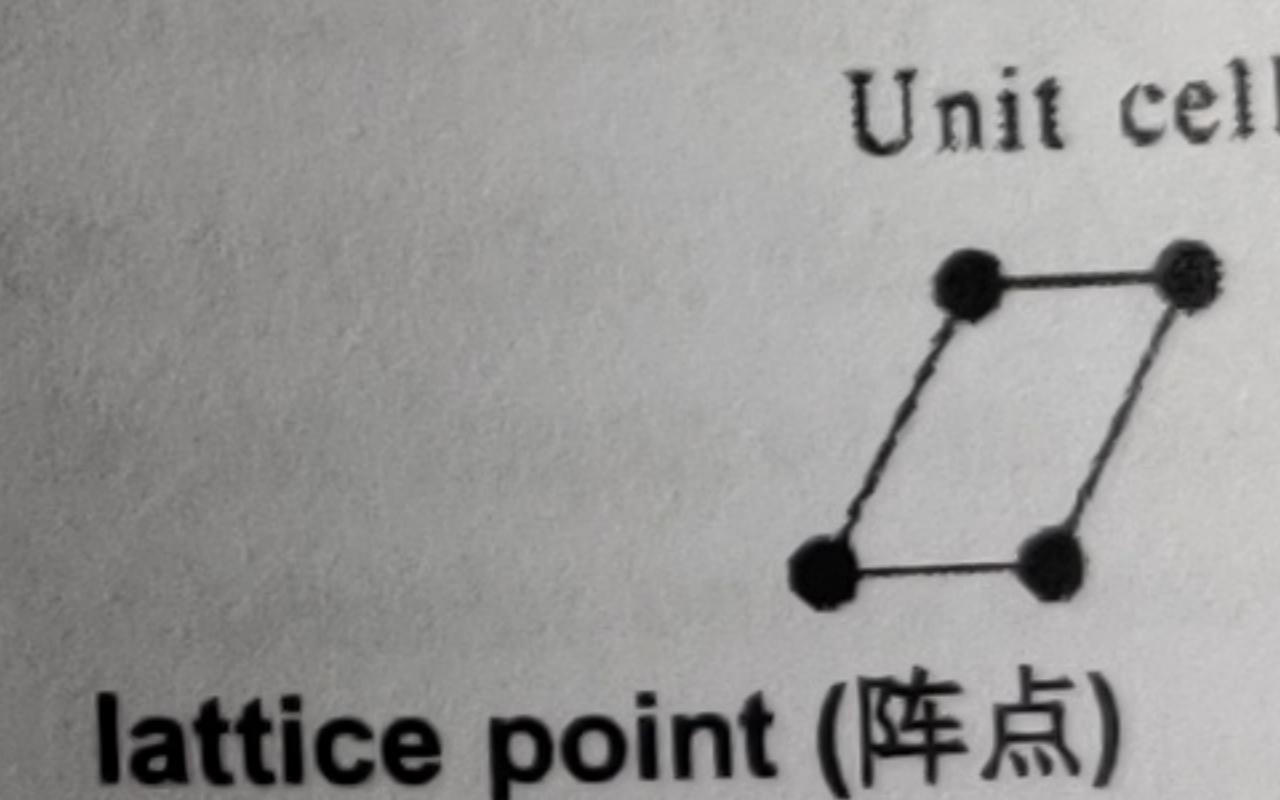
Unit cell: (晶胞)

the smallest repeating unit having the full symmetry of the crystal structure

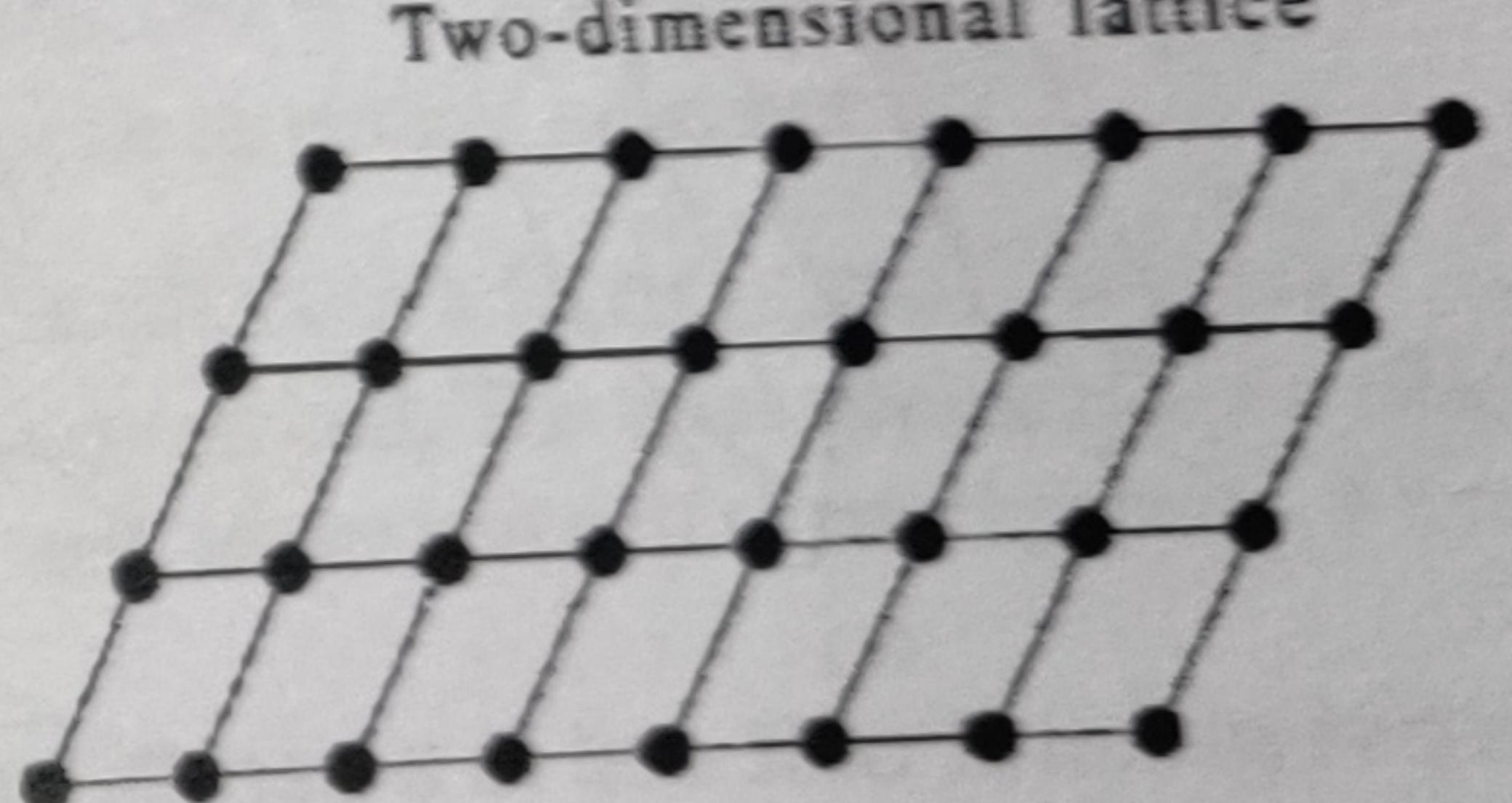


Generation of a crystal lattice (点阵) by a unit cell

Two-dimensional lattice



- Can an unit cell
- ◆ be spherical?
 - ◆ have a five-fold symmetry axis?



An unit cell can NOT be arbitrary shape
must be a structure that fills all space when replicated

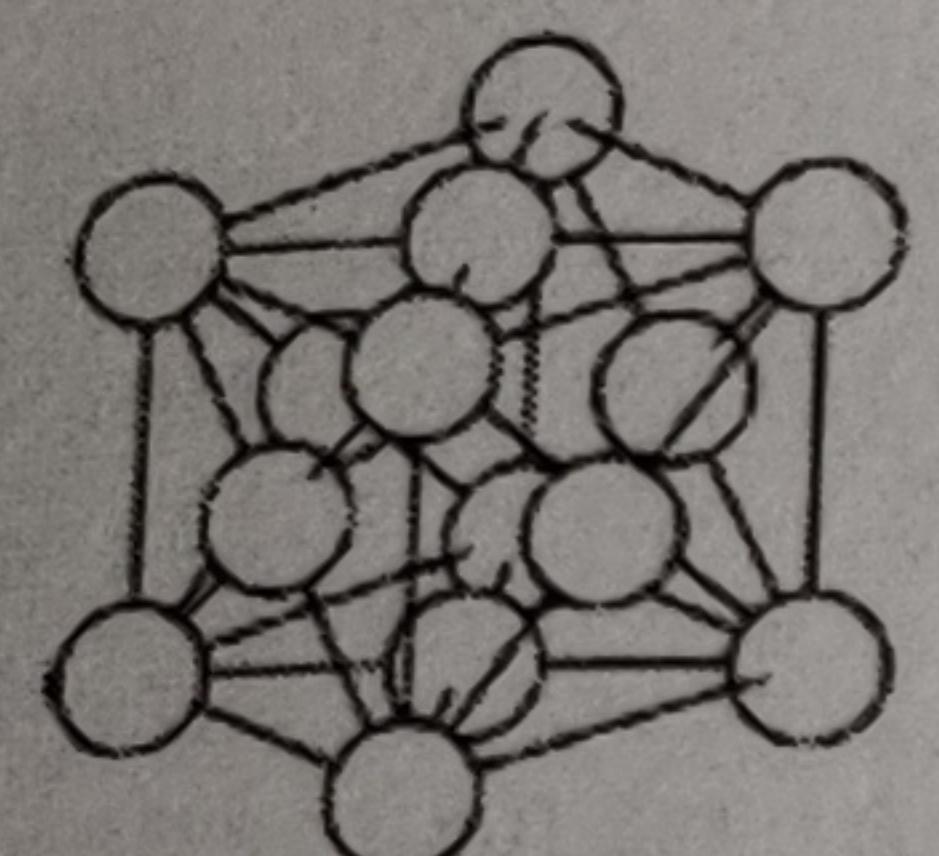
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Cubic Unit Cell: crystalline copper (Cu)

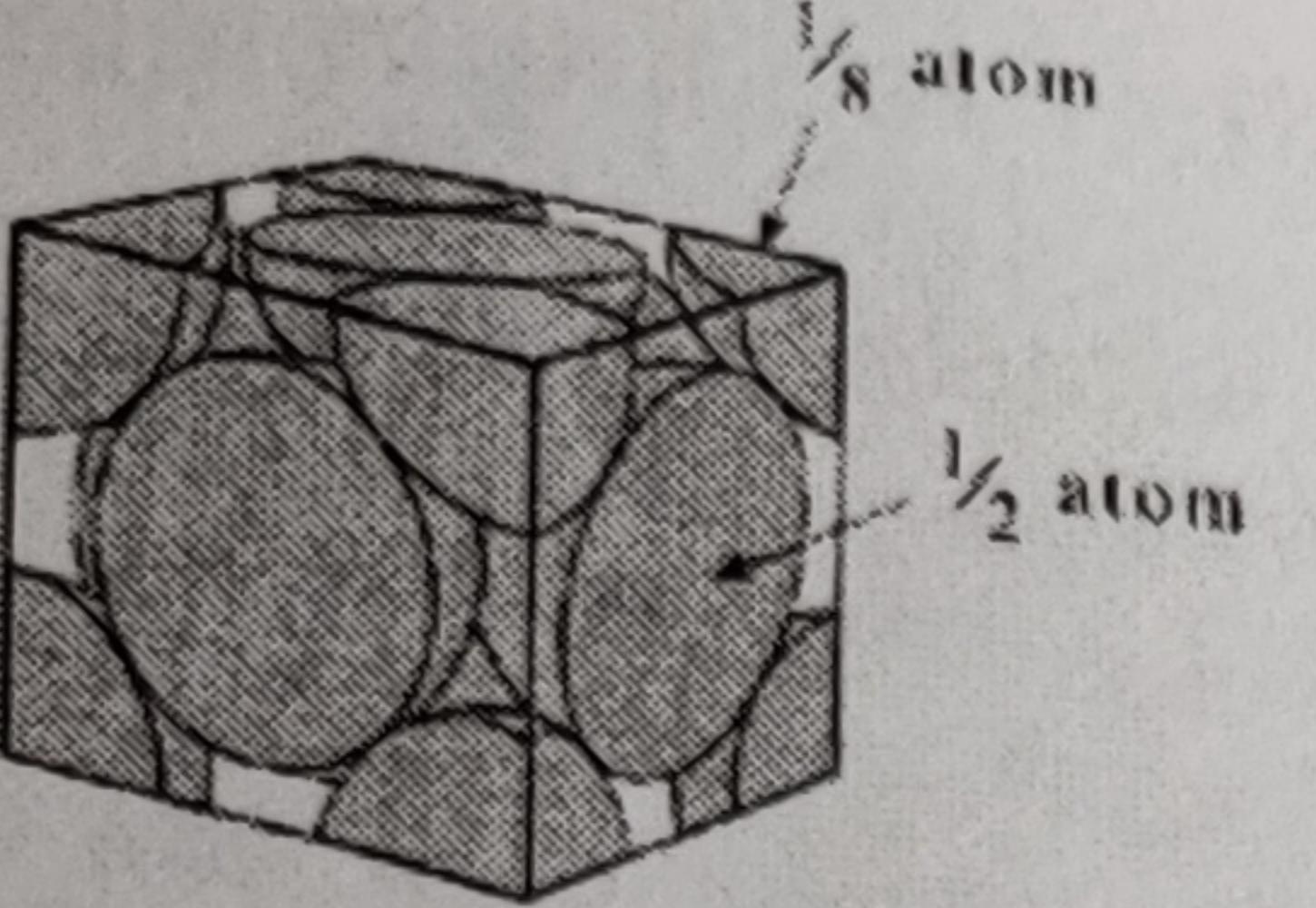


(a)



(b)

face-centered cubic



(c)

Four atoms per unit cell;
atoms touch along a face diagonal

How many atoms per unit cell?

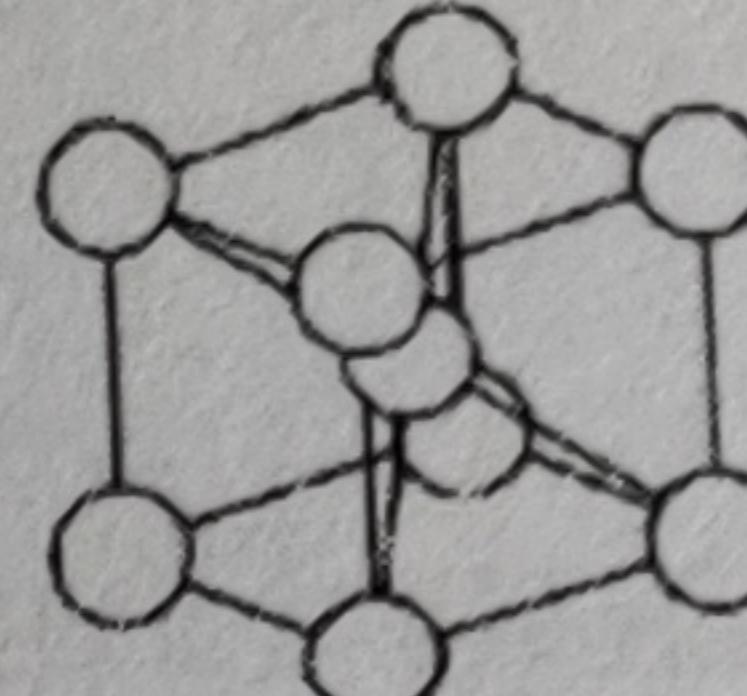
$$8 \text{ (corner)} + 6 \text{ (face)} = 14 ? \quad \times$$

$$(1/8)*8 + (1/2)*6 = 4 \quad \checkmark$$

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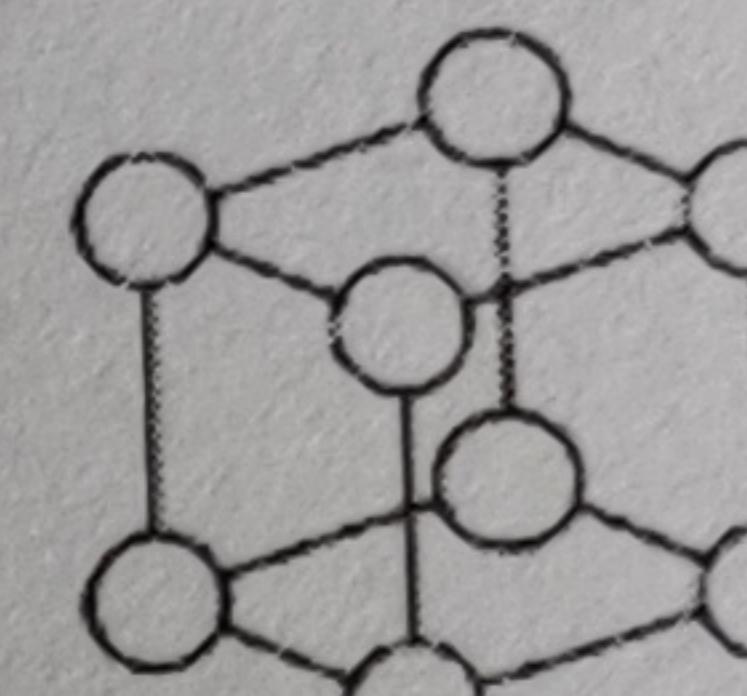
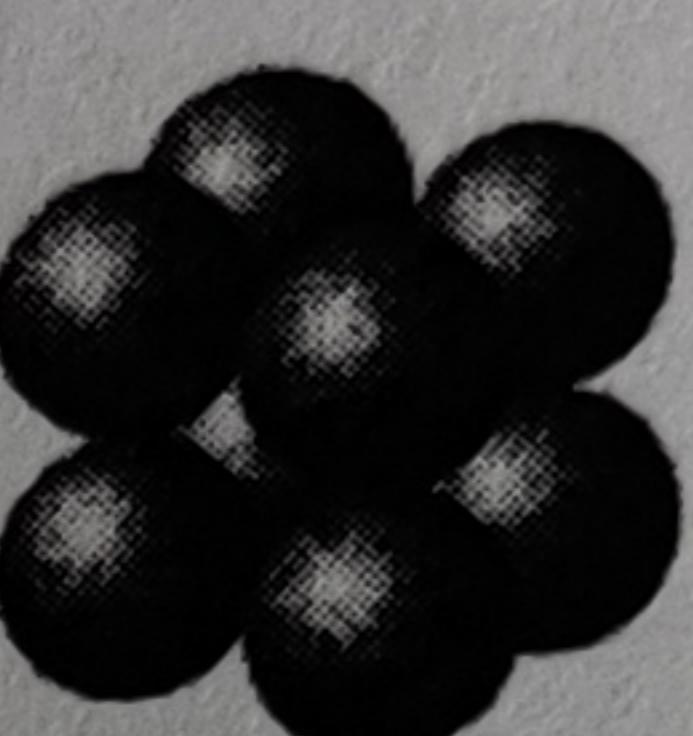
Two Another Cubes



**potassium (K) crystal:
body-centered cubic**

Two atoms per unit cell;
atoms touch along the main diagonal

$\frac{1}{8}$ atom



**Polonium (Po) crystal:
primitive cubic
(only for Po)**

One atom per unit cell;
atoms touch along edge of the cube

$\frac{1}{8}$ atom

(a)

(b)

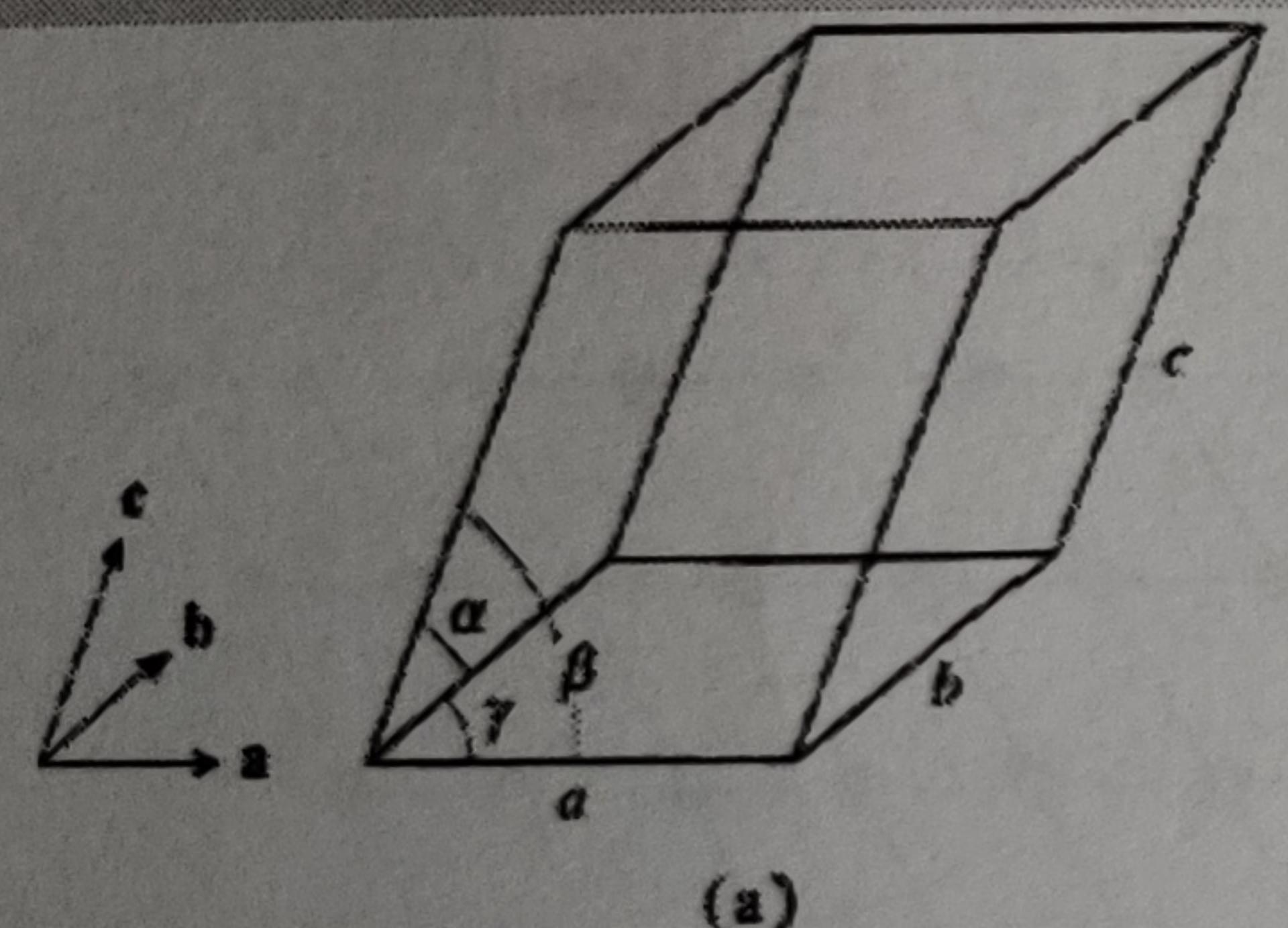
(c)

How many atoms per unit cell?

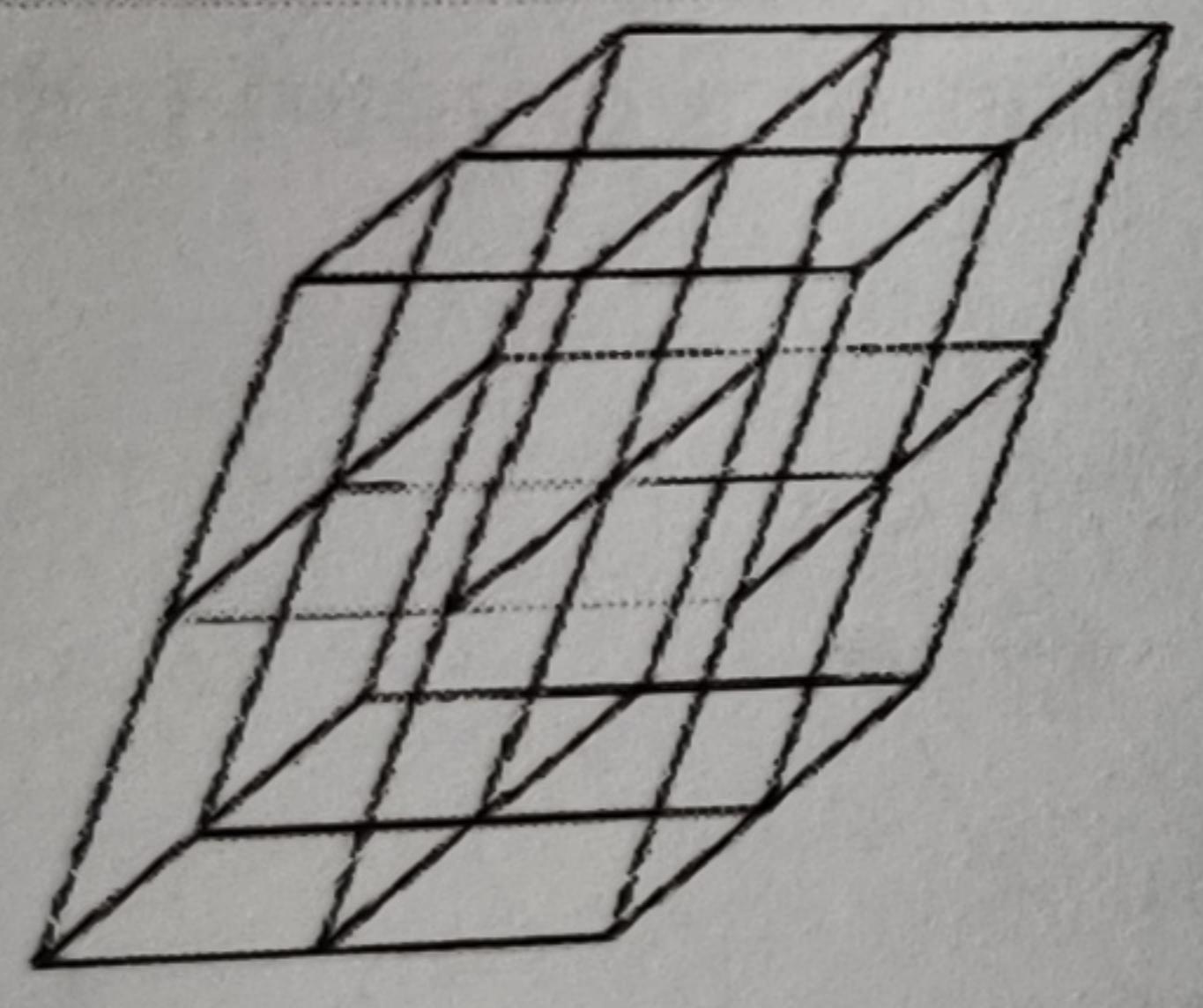
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Must Unit Cells be Cubic?



(a)



(b)

The most general unit cell is a parallelepiped

cell parameters:

The lengths of the principal axes and the angles between them

Infinite Number of Unit Cells?

In 1848, August Bravais (French Physicist) proved that only 14 distinct unit cells are necessary can generate all possible crystal lattices.

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P

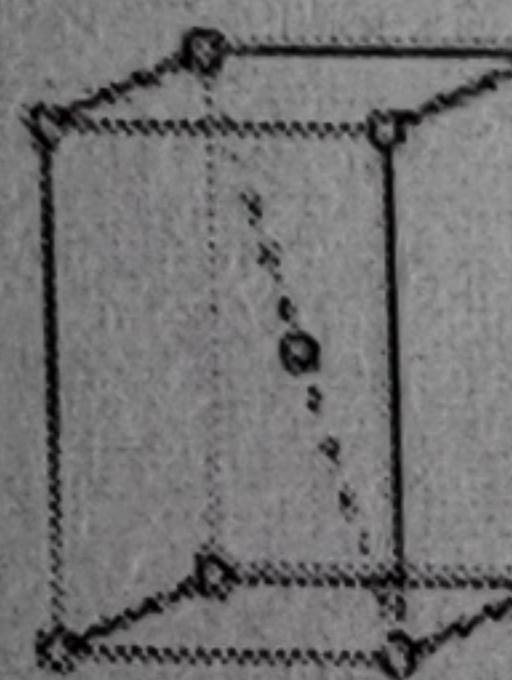
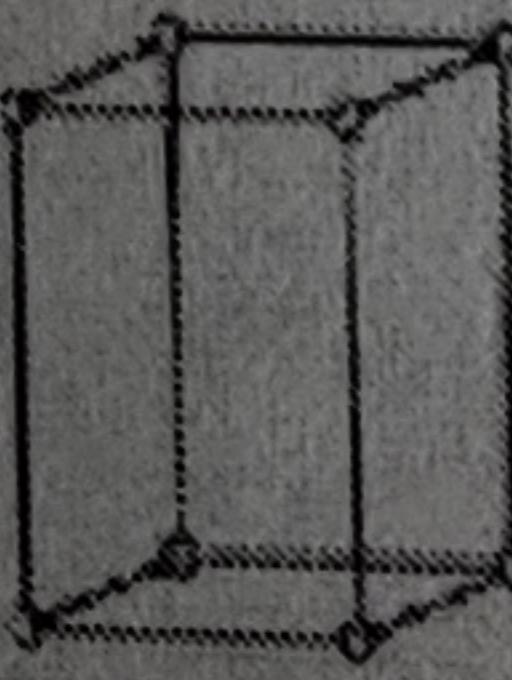
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C

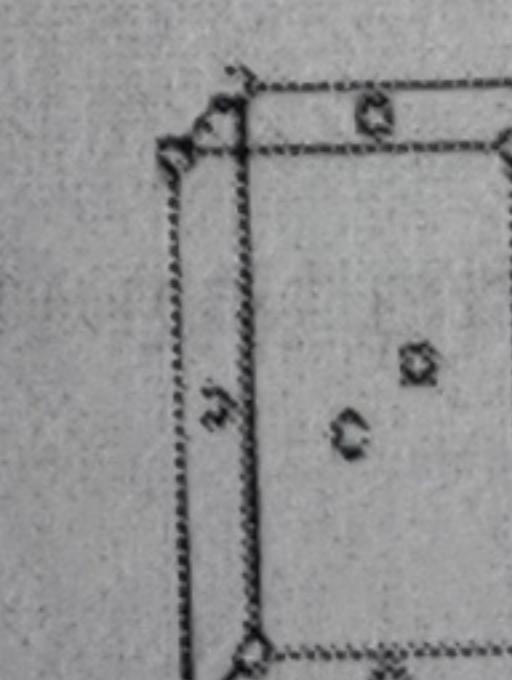
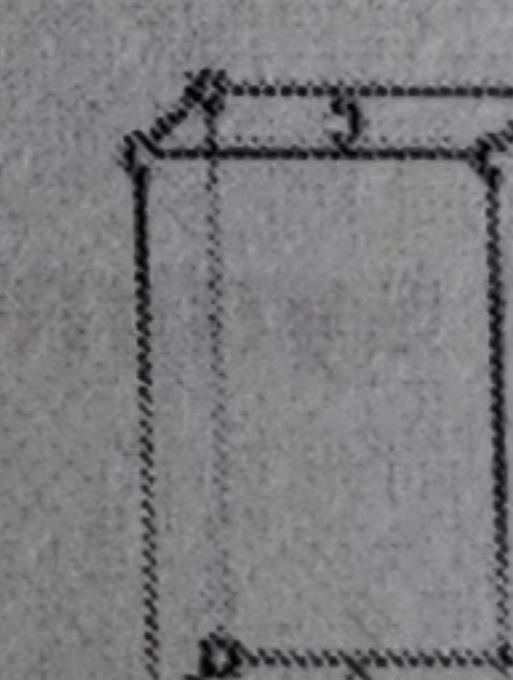
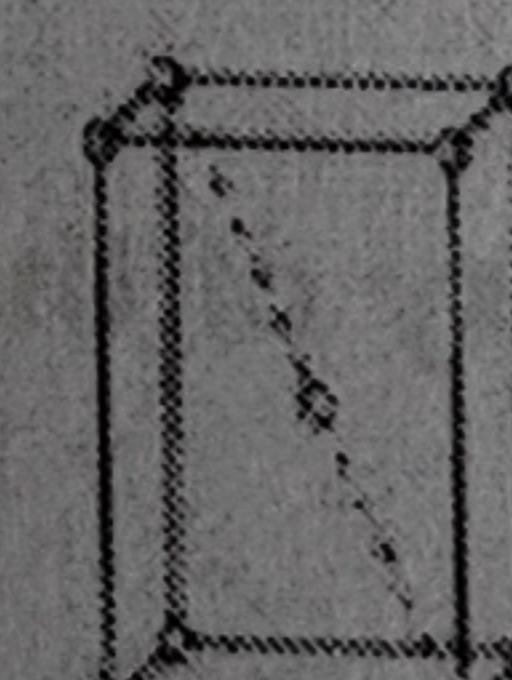
F

R

Triclinic
 $a \neq b \neq c$
 $\alpha \neq \beta \neq \gamma$



Monoclinic
 $a \neq b \neq c$
 $\gamma \neq \alpha = \beta = 90^\circ$



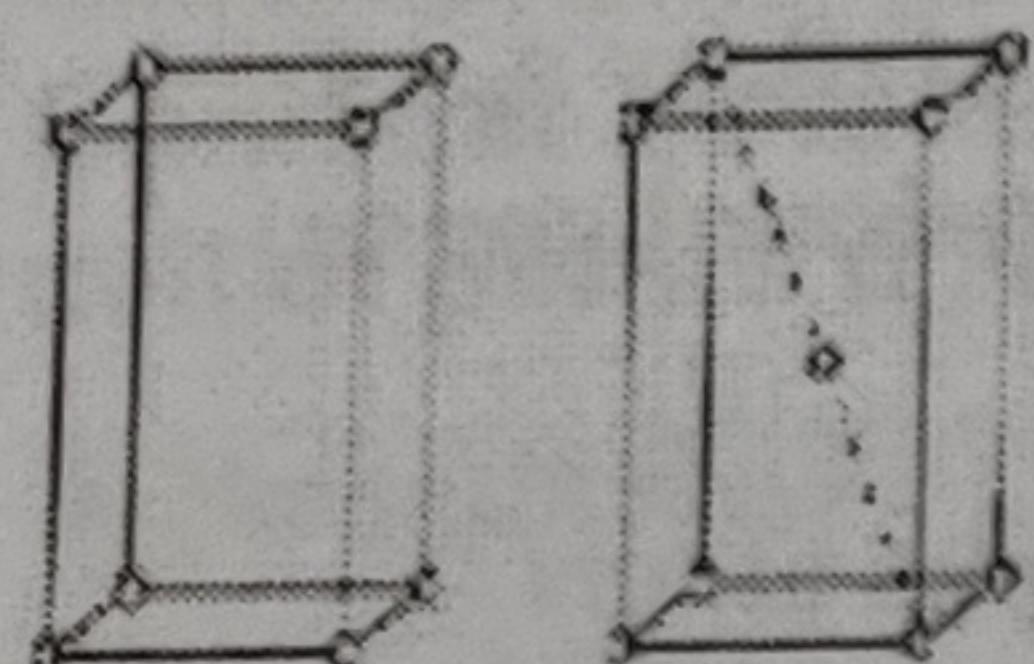
Orthorhombic
 $a \neq b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



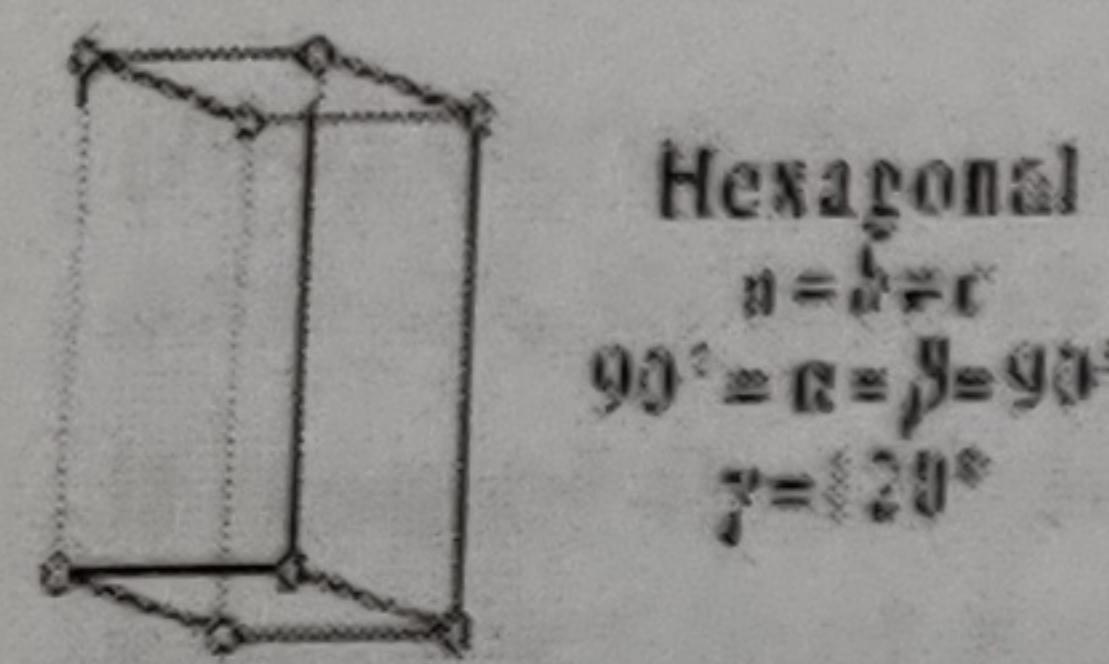
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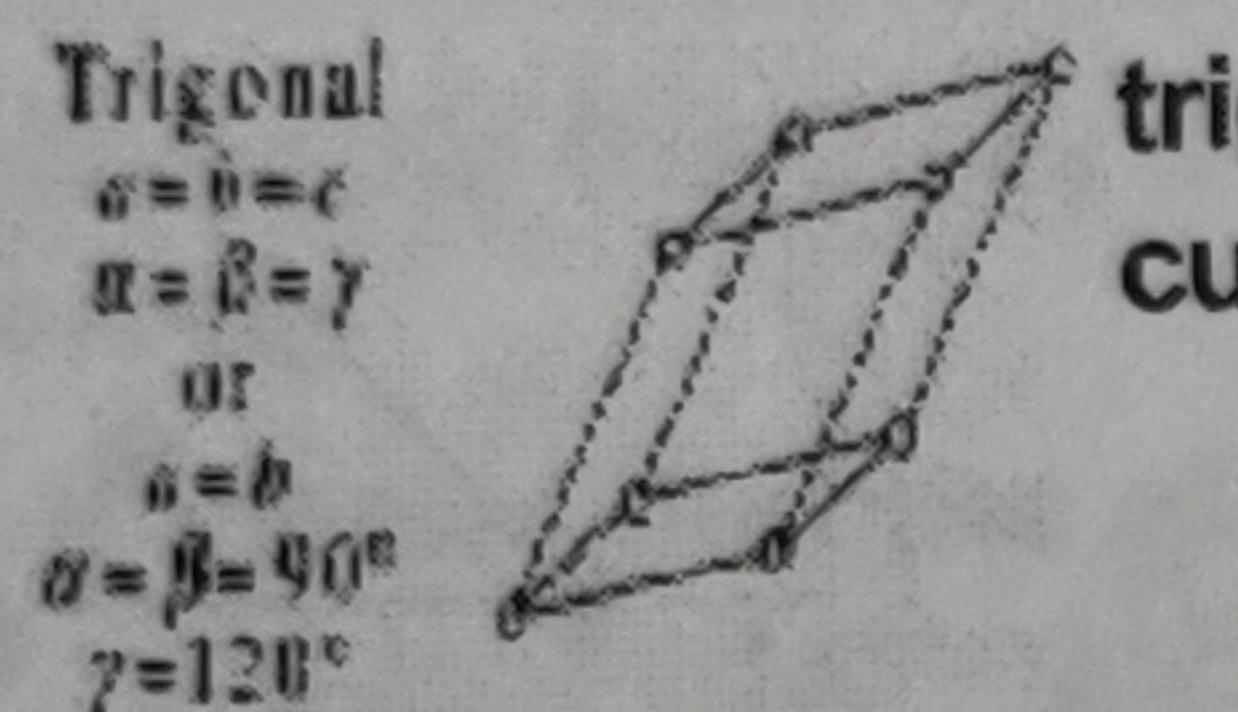
P I C F R



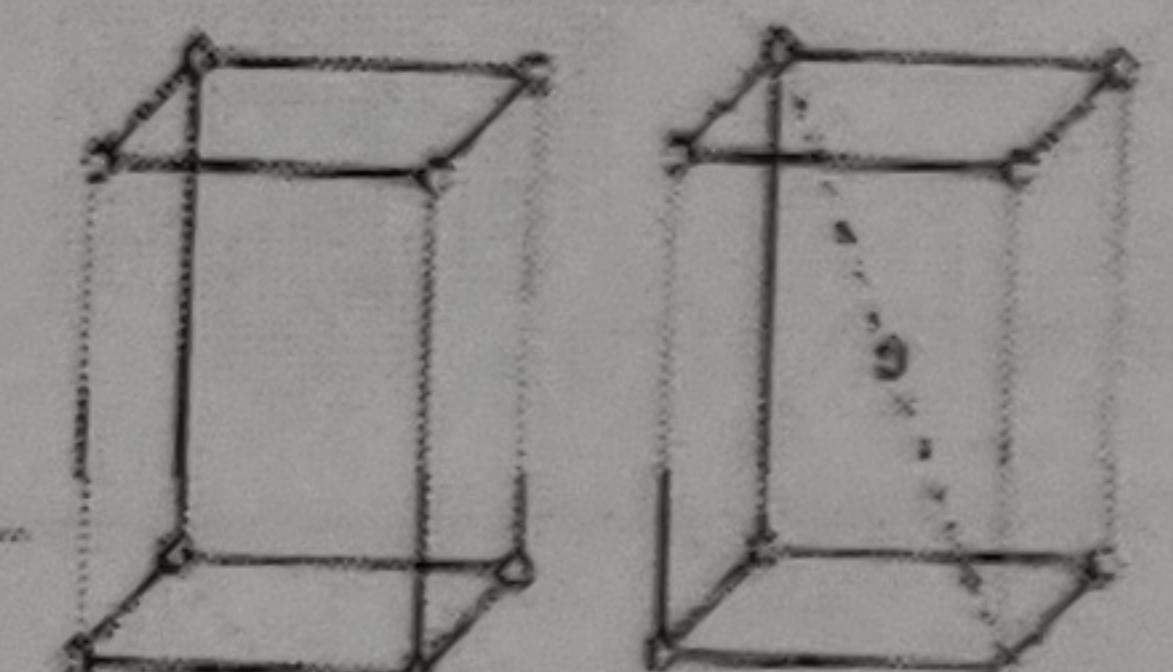
Tetragonal
 $a = b \neq c$
 $\alpha = \beta = \gamma = 90^\circ$



Hexagonal
 $a = b \neq c$
 $90^\circ = \alpha = \beta = 90^\circ$
 $\gamma = 120^\circ$



Trigonal
 $a = b = c$
 $\alpha = \beta = \gamma$
or
 $a = b$
 $\alpha = \beta = 90^\circ$
 $\gamma = 120^\circ$



Cubic
 $a = b = c$
 $\alpha = \beta = \gamma = 90^\circ$

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Because the unit cell is cubic, a , the length of an edge, is given by the cube root of $V_{\text{unit cell}}$, or

$$a = (V_{\text{unit cell}})^{1/3} = 3.616 \times 10^{-8} \text{ cm} = 361.6 \text{ pm}$$

Figure 29.3c shows that the effective radius of an atom in a face-centered cubic lattice is given by one-fourth of the length of the diagonal of a face. The length of the diagonal is given by

$$d = (2)^{1/2}a = 511.4 \text{ pm}$$

so the crystallographic radius of a copper atom is $(511.4 \text{ pm})/4 = 127.8 \text{ pm}$.



EXAMPLE 29-2

Copper, which crystallizes as a face-centered cubic lattice, has a density of $8.930 \text{ g} \cdot \text{cm}^{-3}$ at 20°C . Calculate the radius of a copper atom, assuming that the atoms touch along a face diagonal, as shown in Figure 29.3c. Such a radius is called the *crystallographic radius*.

SOLUTION: There are four atoms per unit cell, so the mass of a unit cell is

$$\text{mass unit cell} = \frac{(4)(63.55 \text{ g} \cdot \text{mol}^{-1})}{6.022 \times 10^{23} \text{ mol}^{-1}} = 4.221 \times 10^{-22} \text{ g}$$

and so its volume is

$$V_{\text{unit cell}} = \frac{4.221 \times 10^{-22} \text{ g}}{8.930 \text{ g} \cdot \text{cm}^{-3}} = 4.727 \times 10^{-23} \text{ cm}^3$$

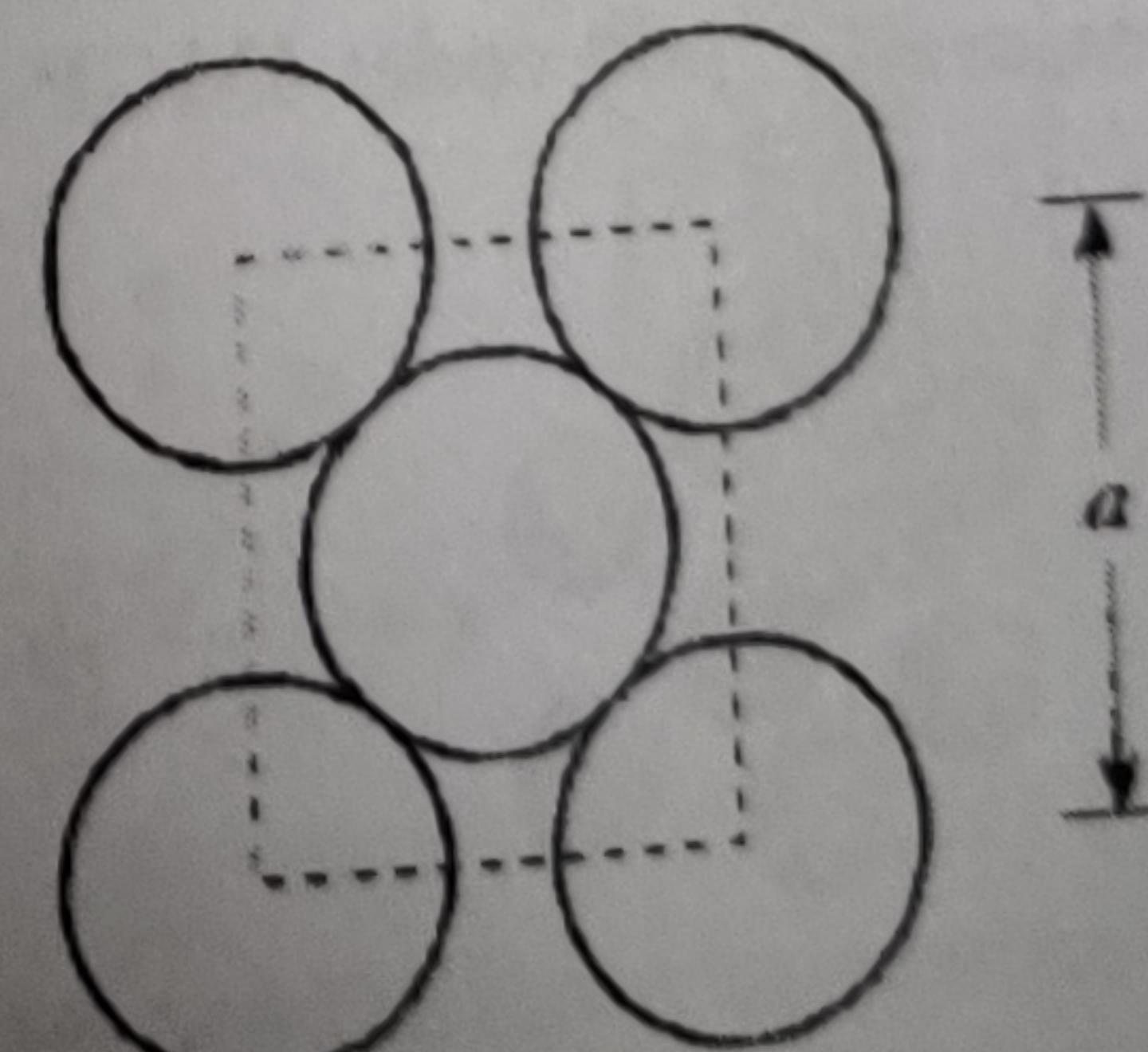
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EXAMPLE 29-3

What fraction of the volume of the unit cell is occupied by copper atoms? Assume each atom is a hard sphere in contact with its nearest neighbor.

SOLUTION: Recall that copper crystallizes in a face-centered cubic structure. Let a be the length of the sides of the cubic unit cell. The total volume of the unit cell is a^3 . Consider one of the six identical faces of the unit cell shown below.



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If r is the radius of a copper atom, then by the Pythagorean theorem, we have

$$(4r)^2 = a^2 + a^2$$

or

$$r = \left(\frac{1}{8}\right)^{1/2} a$$

The volume of a copper atom in terms of a , the length of the unit cell, is then

$$V = \frac{4}{3}\pi r^3 = \frac{\pi a^3}{6(8)^{1/2}}$$

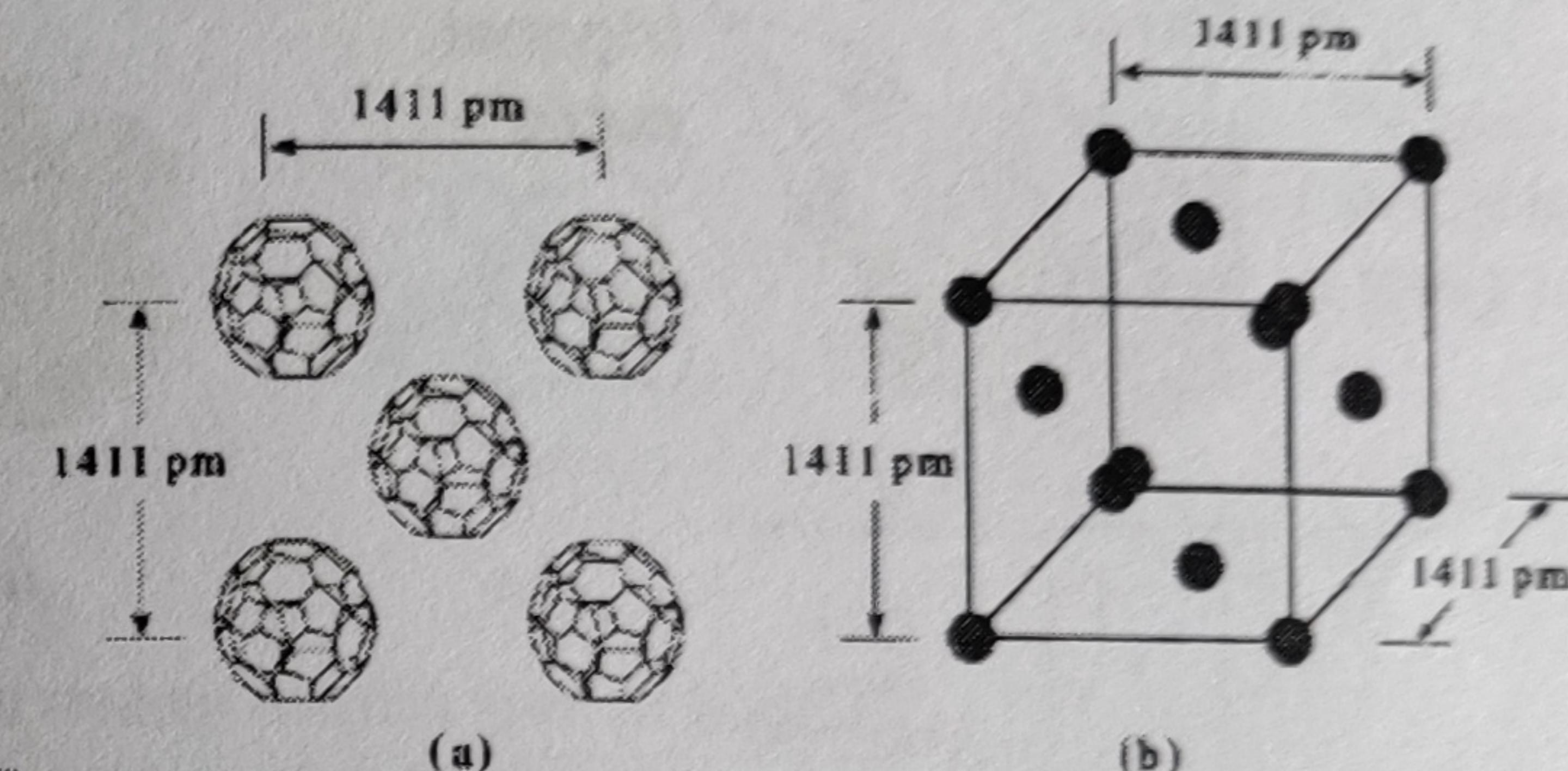
$$\text{fraction occupied} = \frac{4V}{a^3} = 0.740$$

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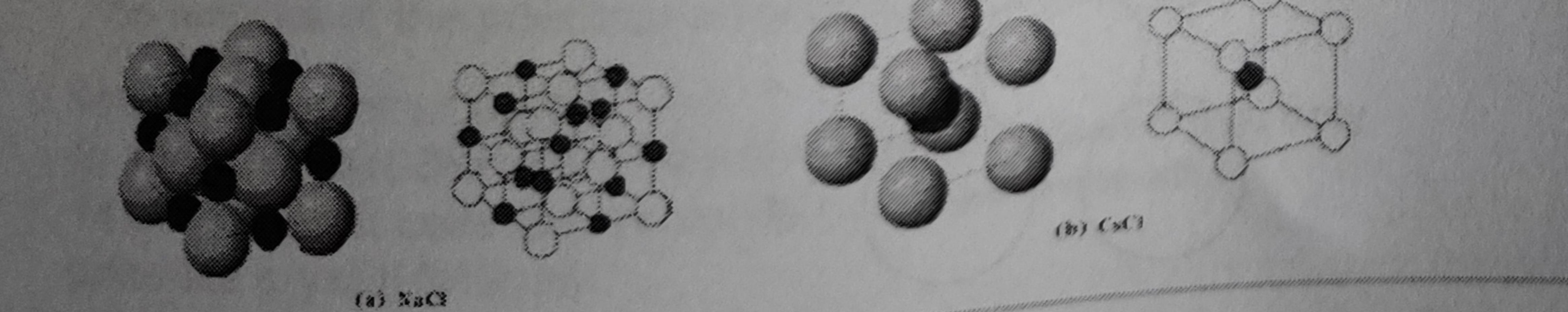
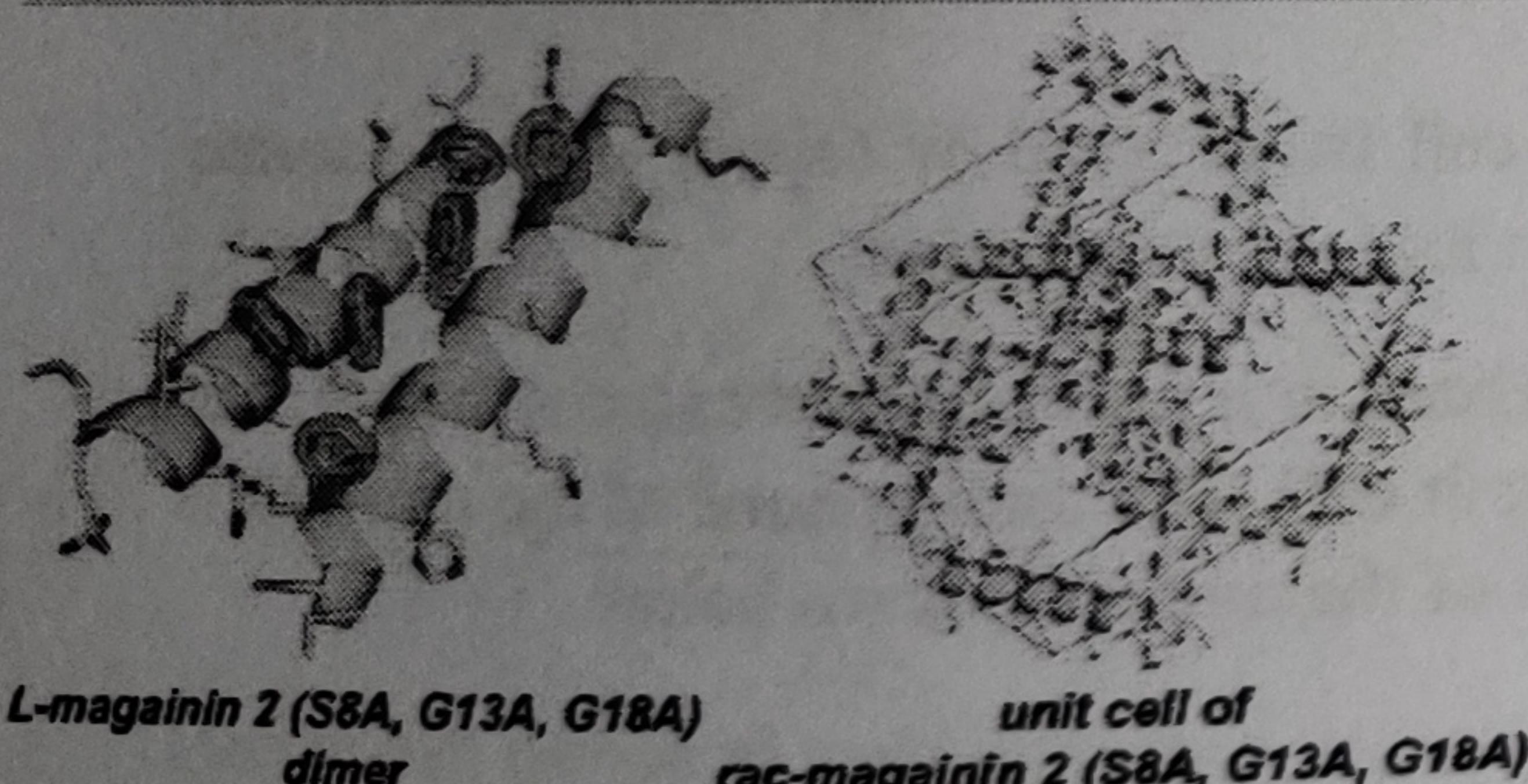


Lattice (点阵): is an infinite array of discrete points generated by a set of discrete translation operations described in three dimensional space
Lattice Points (阵点):

- The points are mathematical constructs; do NOT necessarily depict atoms
- May represent: a single atom, a molecule, a collection of atoms and molecules → molecular crystal. Basis (基元)



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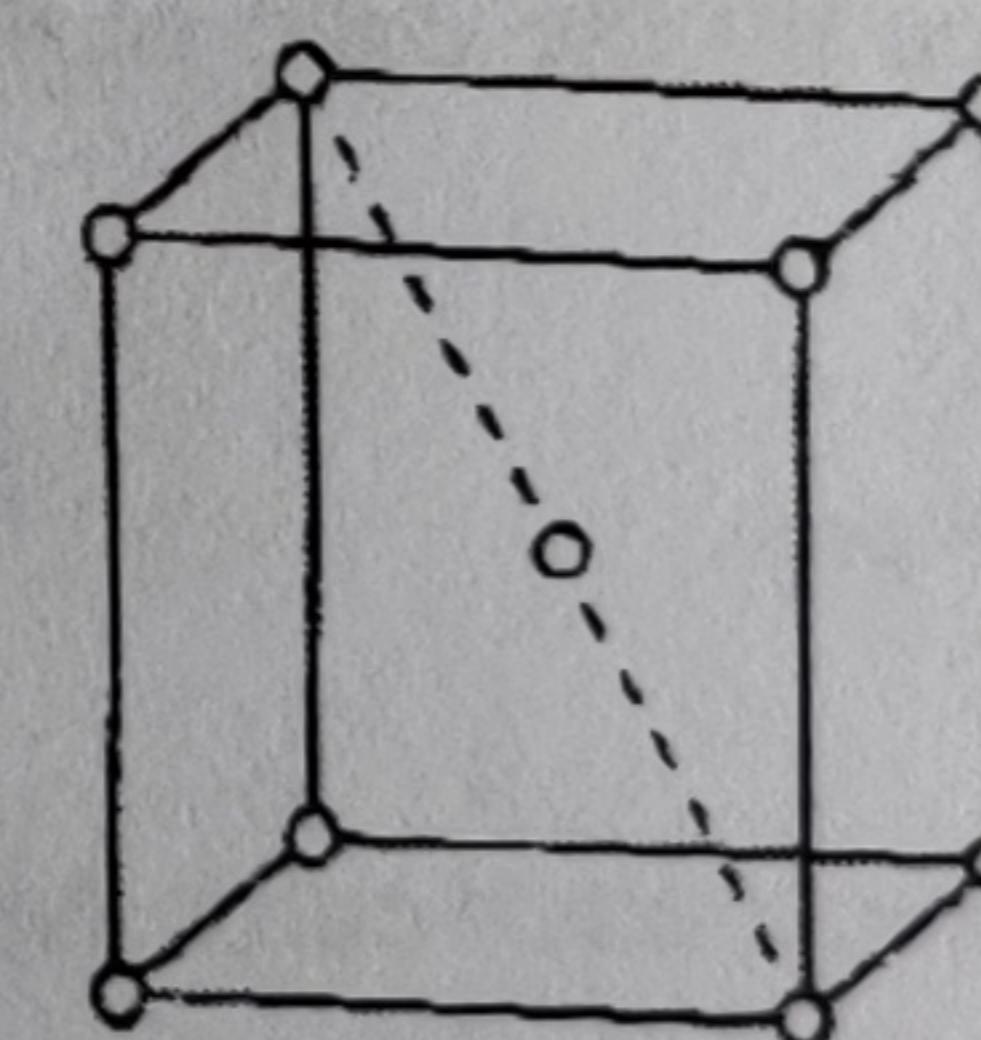


x-ray Crystal Structure of a Magainin 2 Analogue
Hayouka, et al.
J. Am. Chem. Soc. 135,
15738 (2013).
• Protein Data Bank (PDB):
<http://www.rcsb.org/>
pdb code: 4MGP

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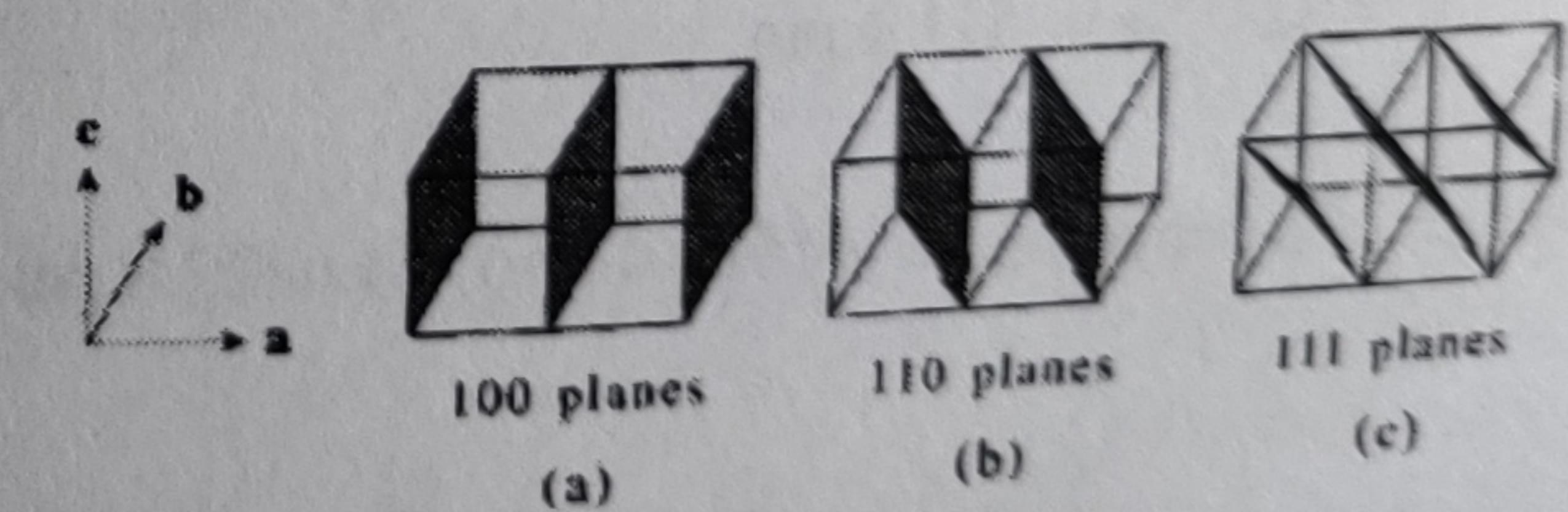
*2. The Orientation of a Lattice Plane Is Described by its Miller Indices



Lattice Points:
primitive cubic:
(0,0,0), (1,0,0), (0,1,0), (0,0,1), (1,1,0),
(1,0,1), (0,1,1), (1,1,1)

body-centered cubic?
Face-centered cubic?

How to denote the Lattice Planes?



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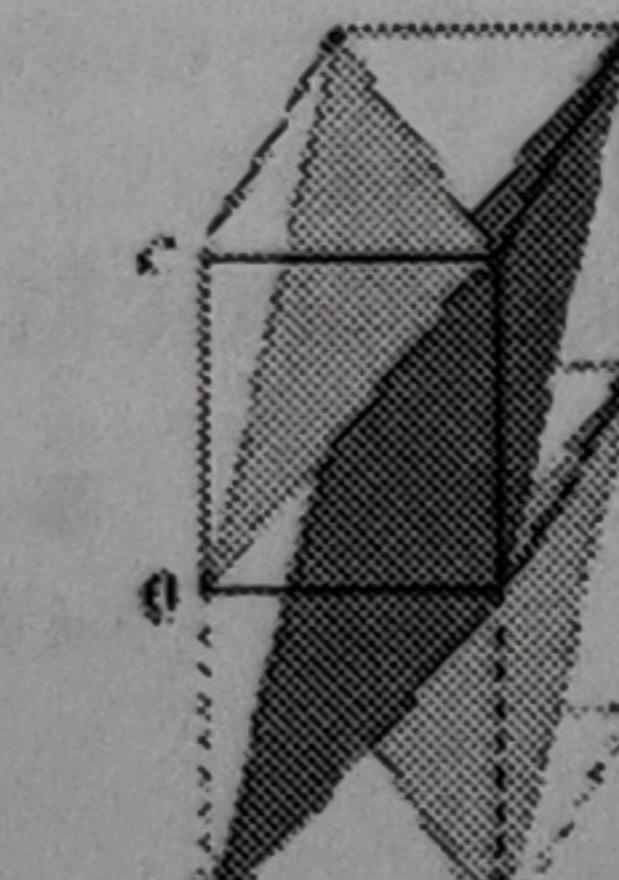
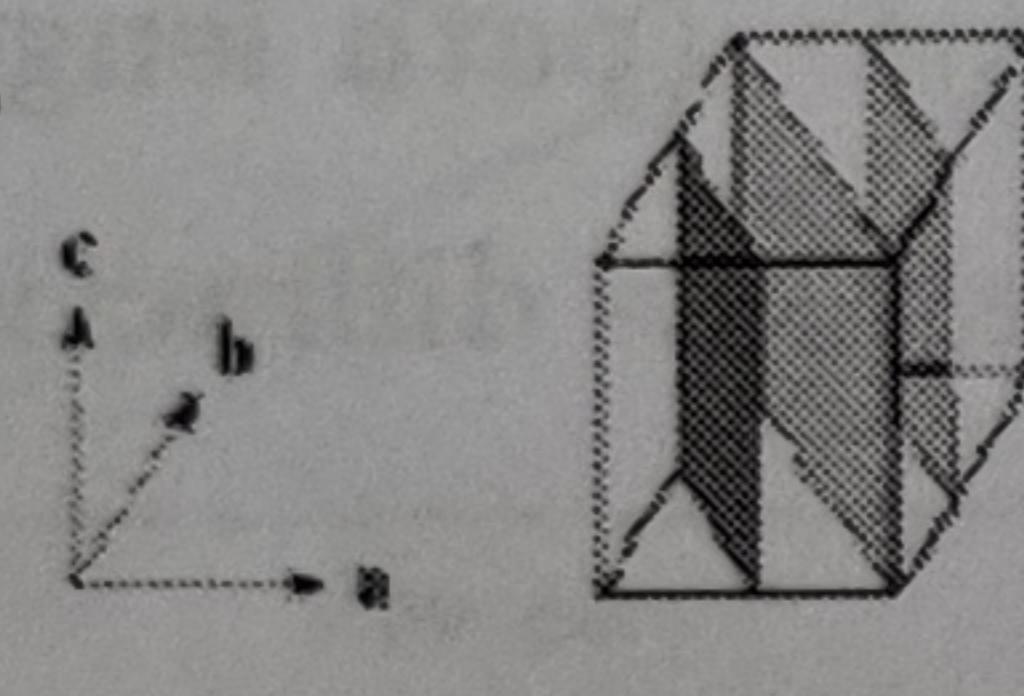
Consider a plane that intersects the a , b , and c axes of a unit cell at points a' , b' , and c'

Miller Indices:

$$h = \frac{a}{a'} \quad k = \frac{b}{b'} \quad l = \frac{c}{c'} \quad (a', b', c' : \text{intersections})$$

(hkl) denotes a plane that intercepts the three points a/h , b/k , and c/l , or some multiple thereof.

If one of the indices is zero, it means that the planes do not intersect that axis.



a family of parallel planes

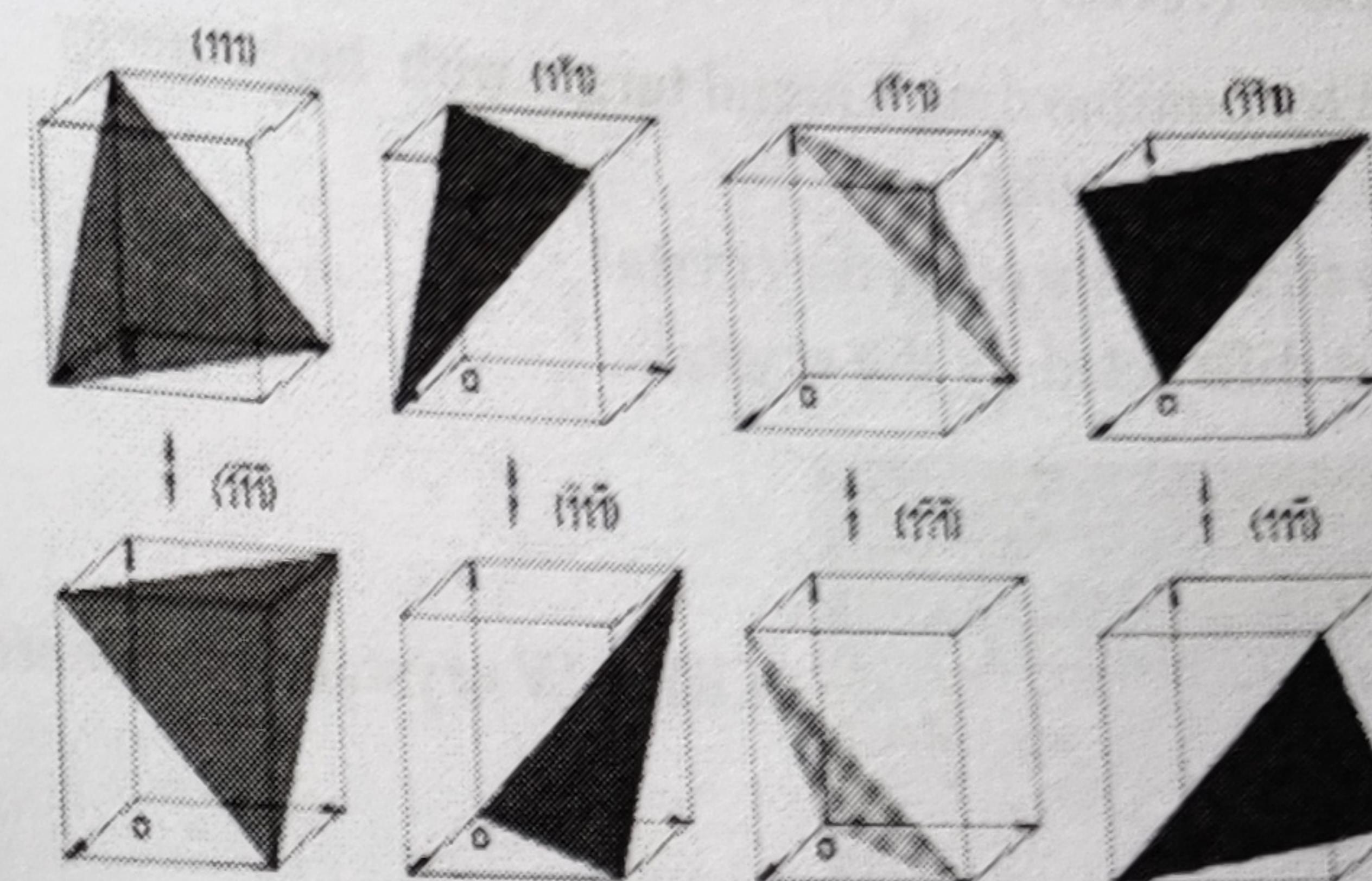
(a)

(b)

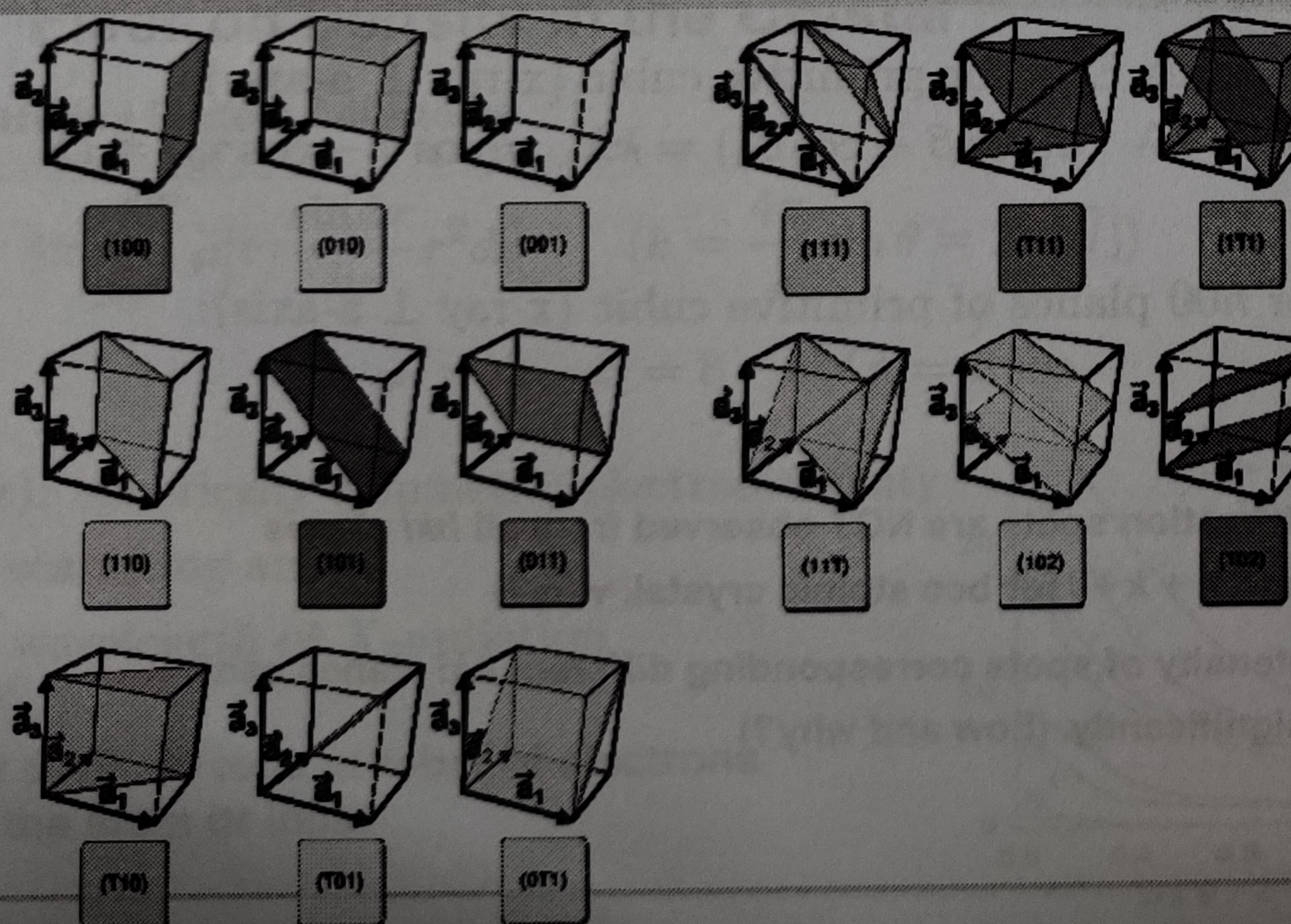
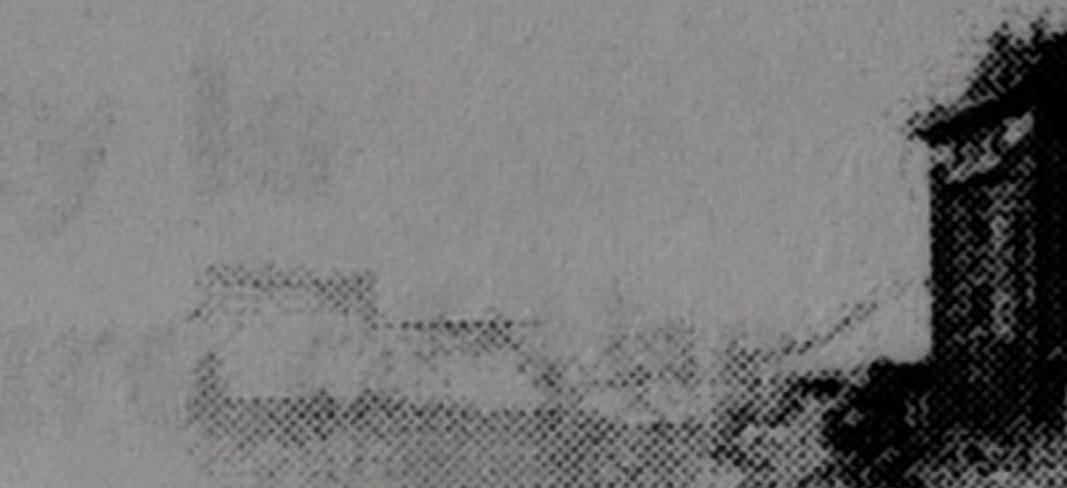
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we designate negative indices by the corresponding number with a bar over it



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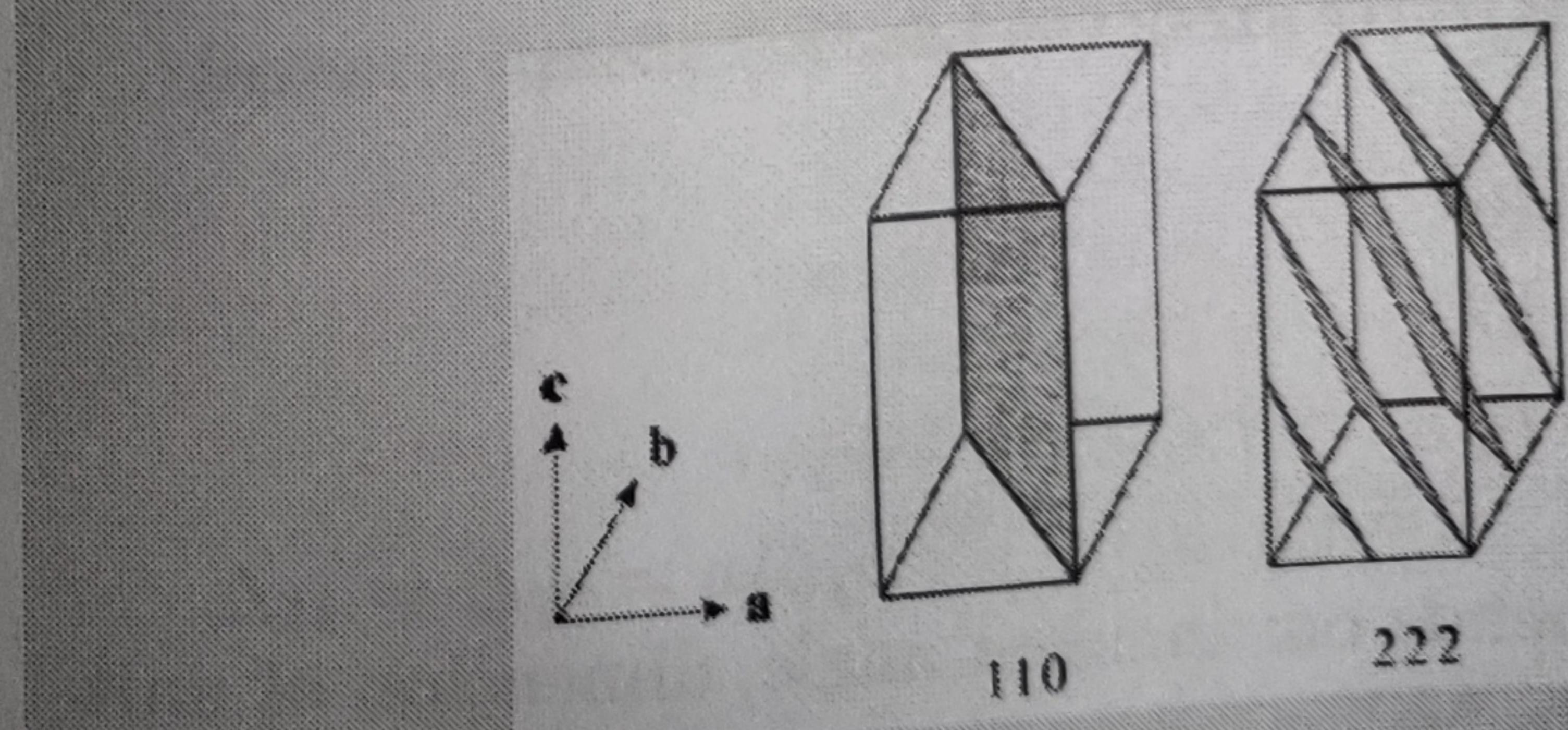


The perpendicular distance between adjacent hkl planes

Orthorhombic unit cell:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Orthorhombic unit cell: $a=437 \text{ pm}$, $b=646 \text{ pm}$, $c=415 \text{ pm}$



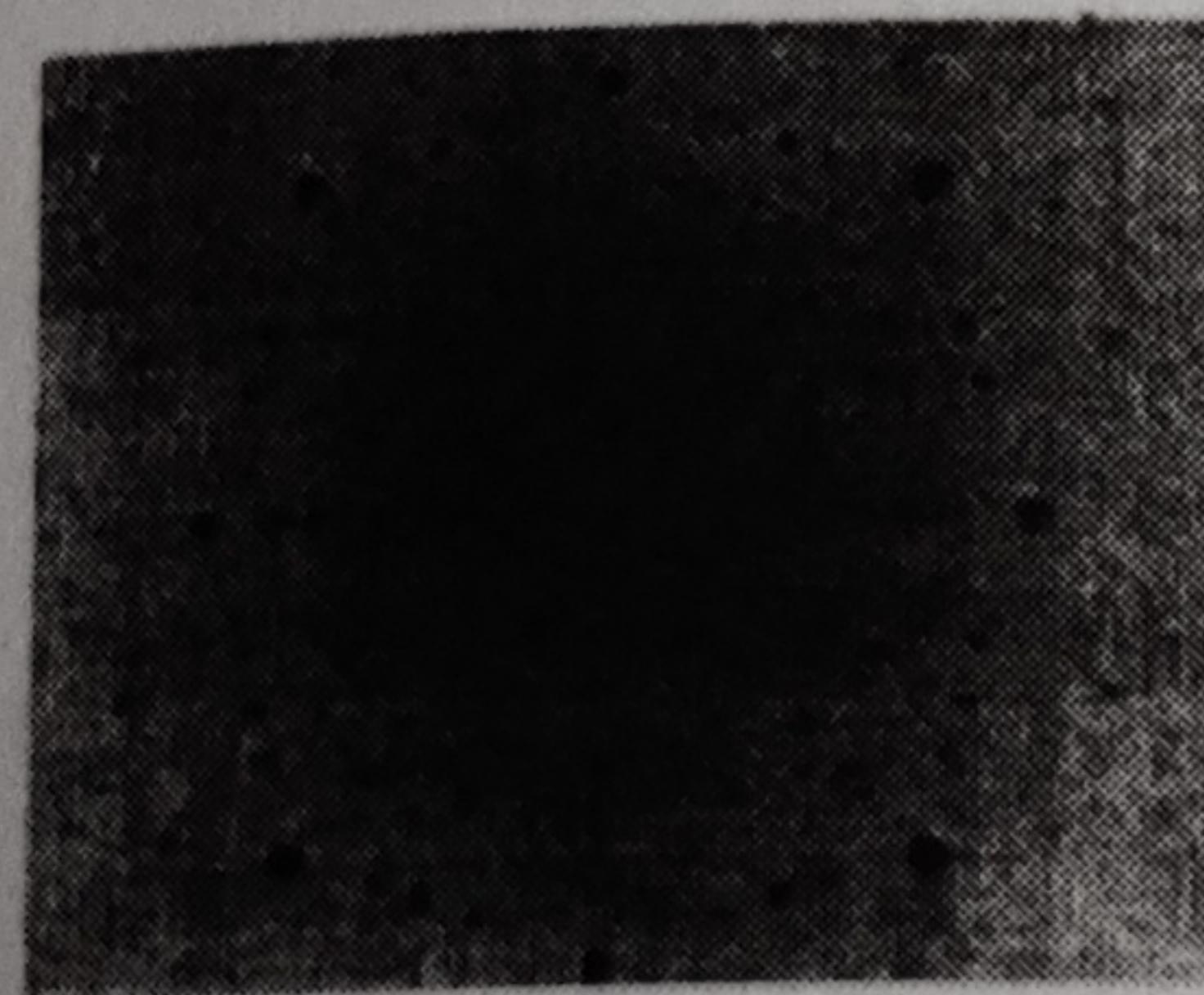
Question: What are the distances between (a) 001, (b) 110 and (c) 222 planes?



3. The Spacing Between Lattice Planes Can Be Determined from X-Ray Diffraction Measurements

X-Ray Diffraction (XRD)

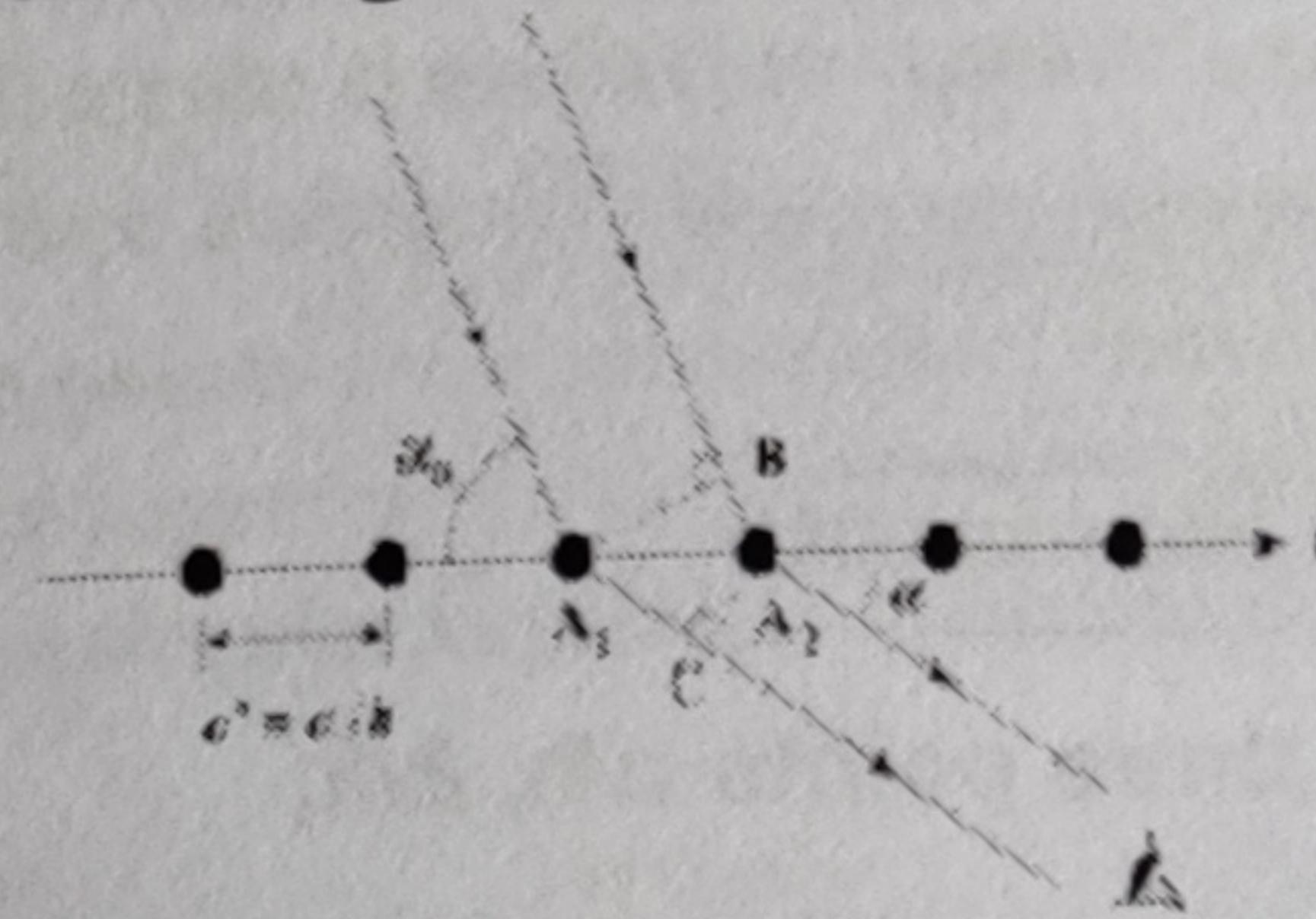
- XRD: generated by bombarding a metal target with high-energy electrons inside a vacuum tube
- Most x-rays pass straight through the crystal
- A small amount is diffracted by the crystal



XRD - W crystal (body-centered cubic)



Scattering from Lattice Points



$$\Delta = \overline{A_1 C} - \overline{A_2 B} = a'(\cos \alpha - \cos \alpha_0) \quad (\text{path length difference})$$

$\Delta = n\lambda$ (interfere constructively \rightarrow diffraction signal)

$$a(\cos \alpha - \cos \alpha_0) = nh\lambda$$

- Positions and intensities of the diffraction spots are determined by the spacing between the different sets of parallel hkl planes of the crystal lattice.

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- von Laue Eqs. for primitive cubic (x-ray \perp a-axis):
 $a \cos \alpha = h\lambda$ $a(\cos \beta - \cos \beta_0) = k\lambda$ $a(\cos \gamma - \cos \gamma_0) = l\lambda$

- For $h00$ planes of primitive cubic (x-ray \perp a-axis):
 $\cos \alpha = h\lambda/a$ $\beta = \beta_0$ $\lambda = \lambda_0$

Q1: Diffraction spots are NOT observed from all hkl planes
 (e.g. odd $h + k + l$ for bcc atomic crystal, why?)

Q2: Intensity of spots corresponding different hkl planes can vary significantly. (how and why?)

First-order Reflections (three axes): von Laue Equations

$$a(\cos \alpha - \cos \alpha_0) = h\lambda$$

$$b(\cos \beta - \cos \beta_0) = k\lambda$$

$$c(\cos \gamma - \cos \gamma_0) = l\lambda$$

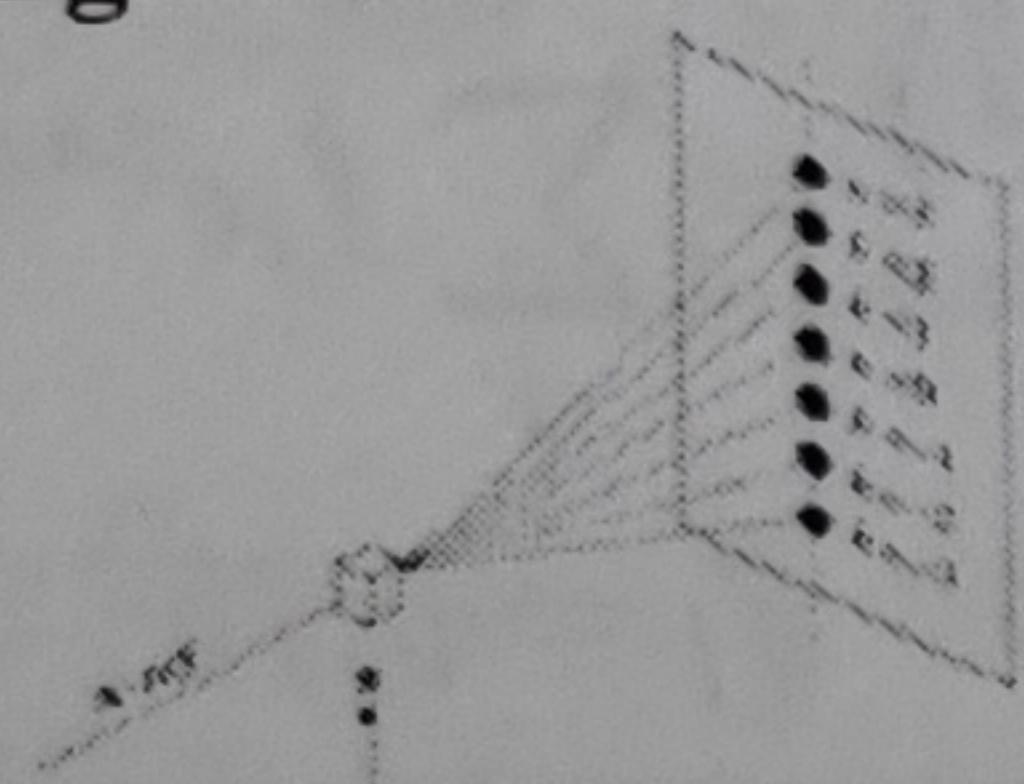
Diffraction angle depends on: incident angle, dimension of unit cell, X-ray wavelength, Miller indices

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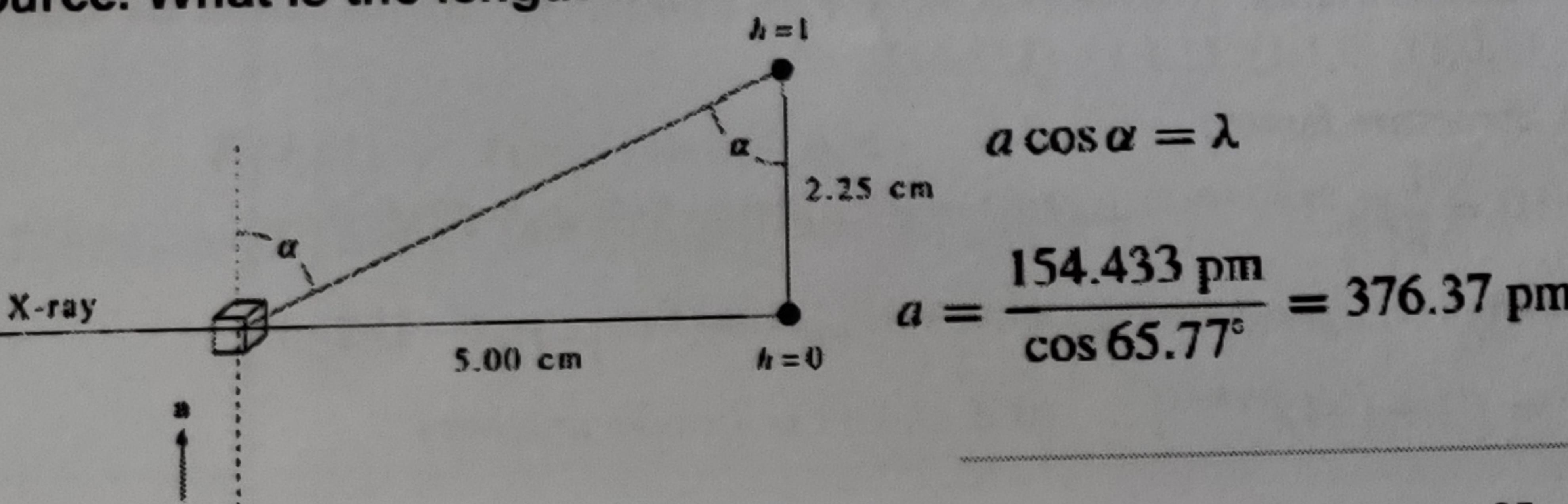
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XRD Scattering from h00 Planes (x-ray \perp a-axis)



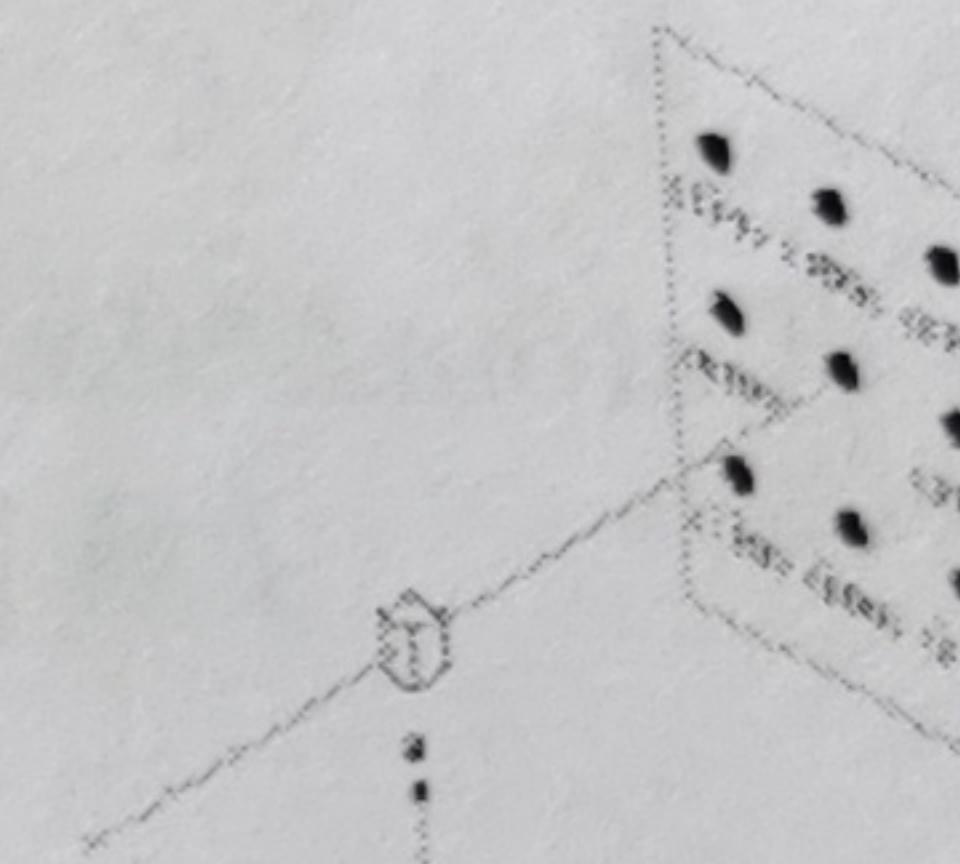
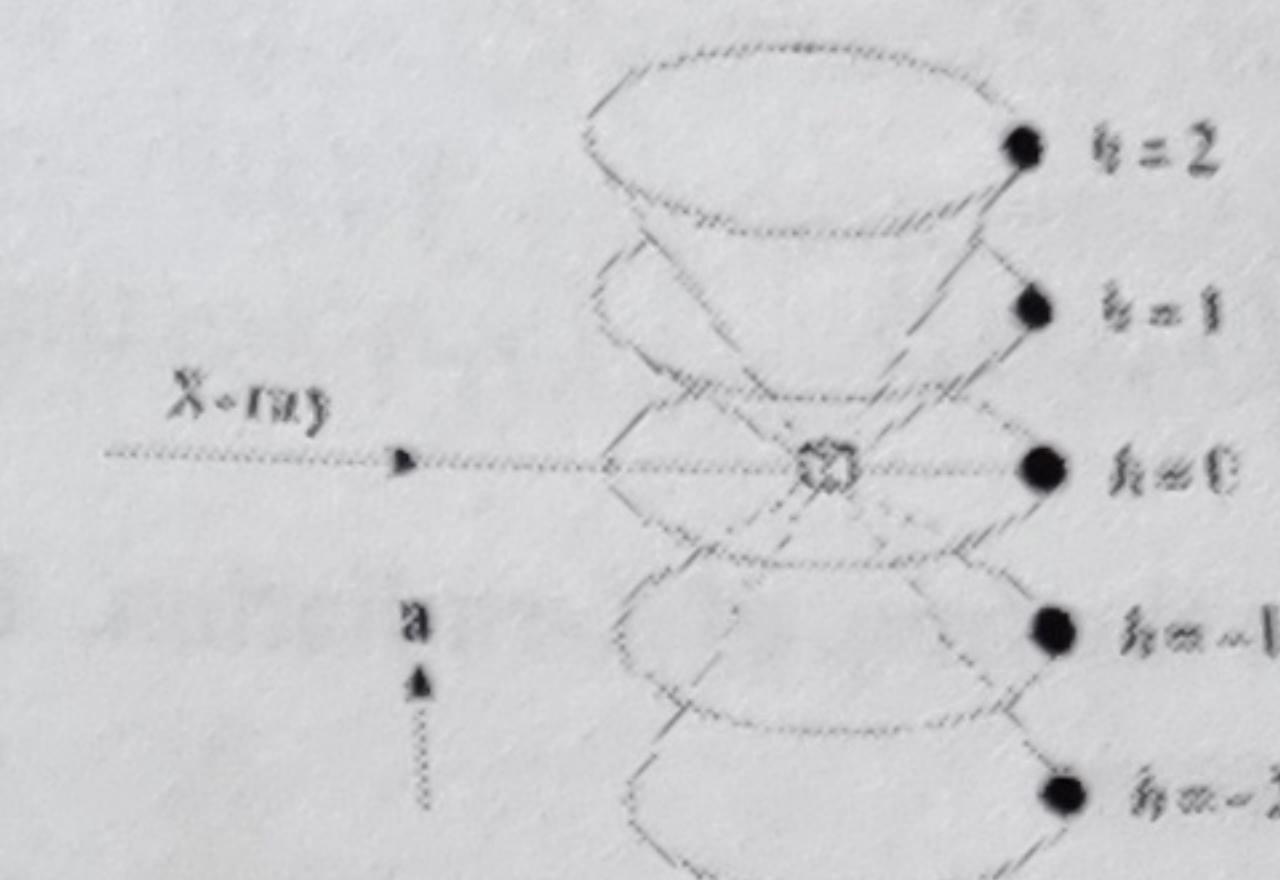
Example: $\lambda = 154.433 \text{ pm}$ line of copper is used as the X-ray source. What is the length of the unit cell along the a axis?



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XRD Scattering from Arbitrary hkl Planes (x-ray \perp a-axis)



Diffraction spots from some planes, primitive cubic, x-ray \perp a-axis

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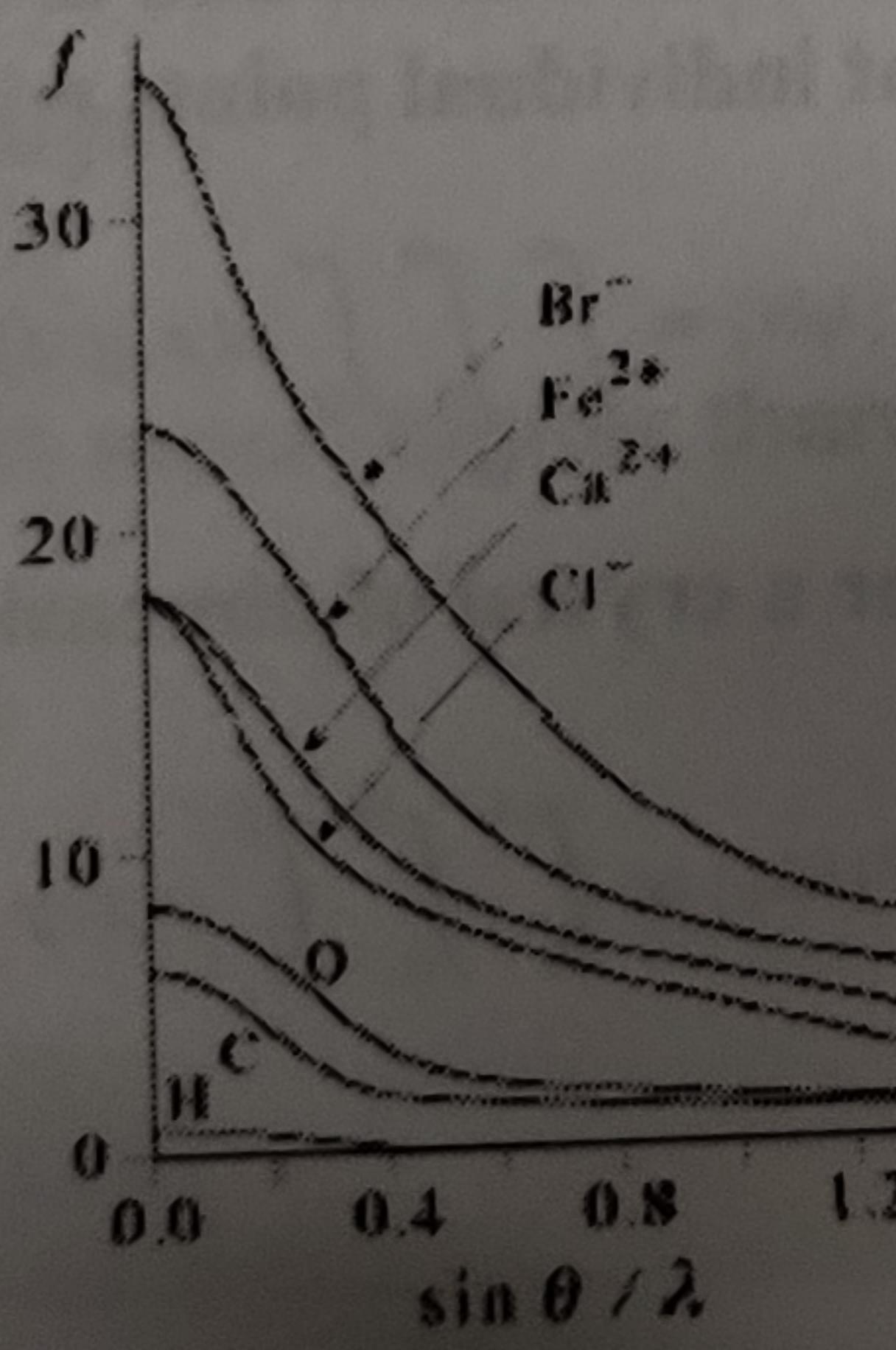
4. The Total Scattering Intensity Is Related to the Periodic Structure of the Electron Density in the Crystal

Scattering Factors f of Atoms

$$f = 4\pi \int_0^{\infty} \rho(r) \frac{\sin kr}{kr} r^2 dr \quad (k = \frac{4\pi}{\lambda} \sin \theta = 2\pi |\vec{H}|)$$

- $\rho(r)$: spherically symmetric electron density
- θ : scattering angle
- λ : wavelength of X-radiation

For $\theta = 0$, $f = \text{total number of electrons on the atom or ions}$



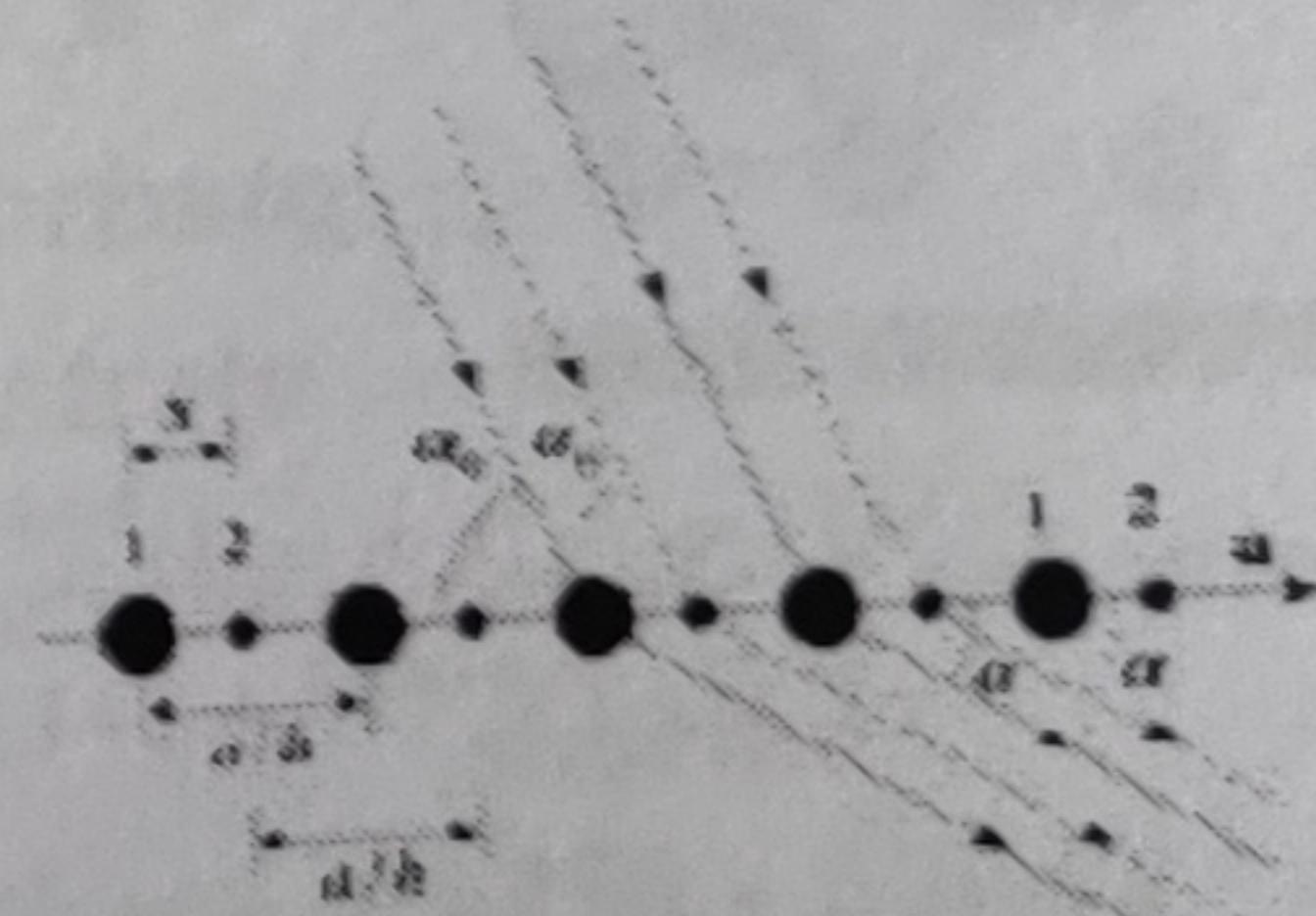
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Scattering Intensity: One-dimension Lattice

Scattering from different region of an atom interfere with each other

- Scattering factors: f_1, f_2 for atoms 1 and 2
- Distance: $d_{11} = d_{22} = a/h, d_{12} = x$



$$\Delta_{11} = \Delta_{22} = a/h(\cos \alpha - \cos \alpha_0) = \lambda \quad (n = 1)$$

$$\Delta_{12} = x(\cos \alpha - \cos \alpha_0) \quad \phi = 2\pi \Delta_{12}/\lambda = 2\pi hx/a \quad (\text{phase difference})$$

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$$A = f_1 \cos \omega t + f_2 \cos(\omega t + \phi) = f_1 e^{i\omega t} + f_2 e^{i(\omega t + \phi)} \quad (\text{amplitude})$$

$$I \propto |A|^2 = f_1^2 + f_2^2 + 2f_1 f_2 \cos \phi \quad (\text{scattering intensity})$$

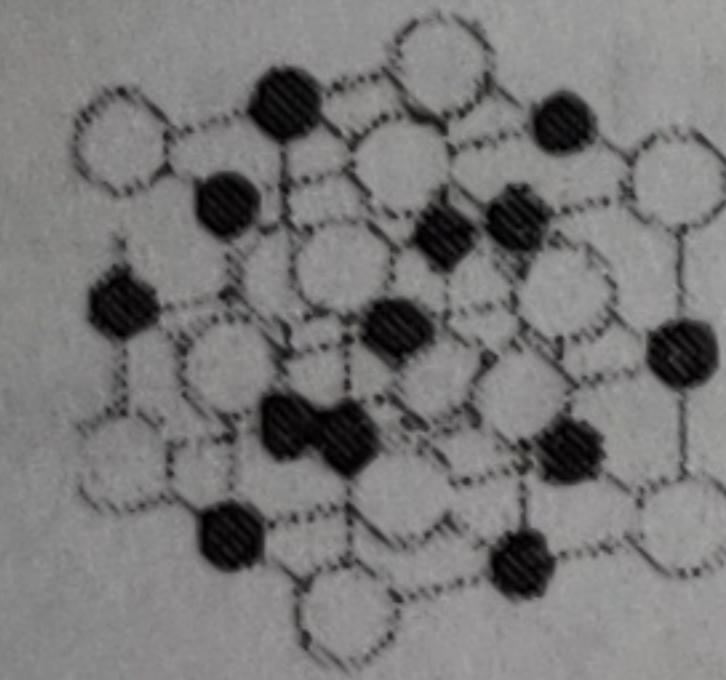
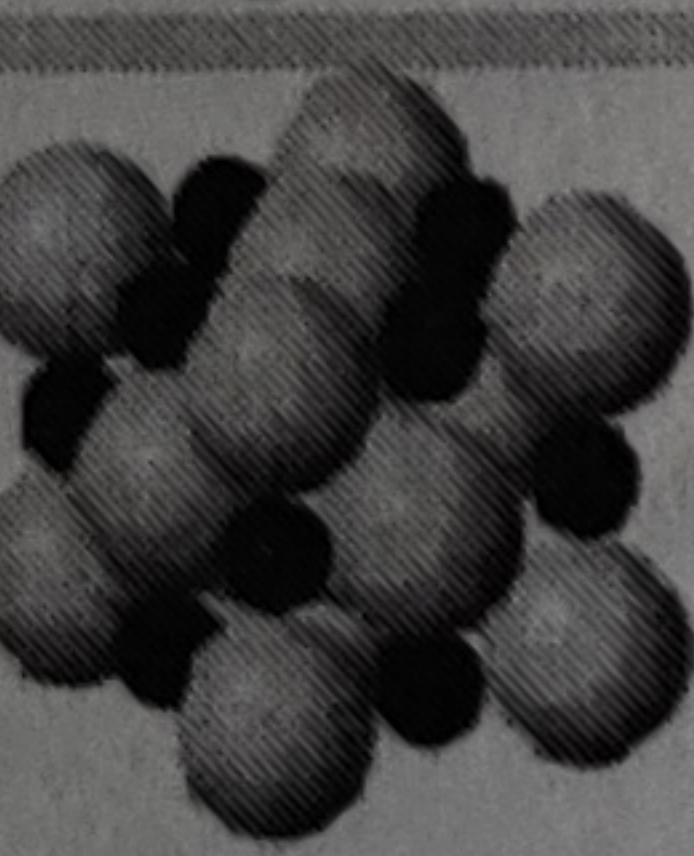
The intensity does NOT depend on the freq. of X-radiation, but depend on the phase difference between the two beams

Structure Factor $F(hkl)$

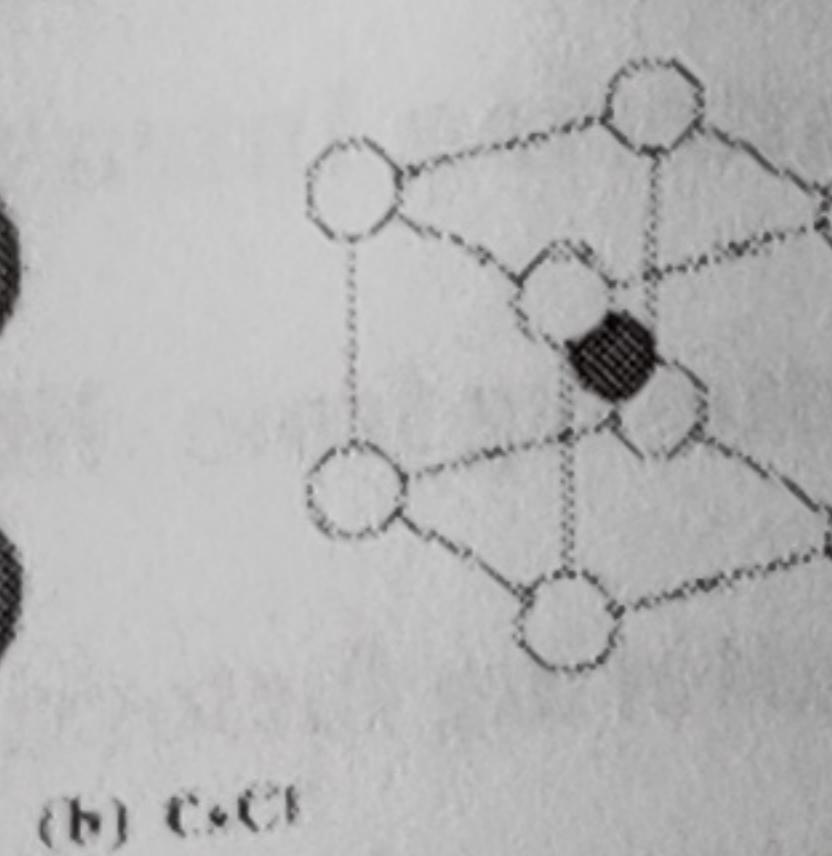
- One-dimension (two types of atoms, along the a axis)

$$F(h) = f_1 + f_2 e^{i\phi} = f_1 + f_2 e^{2\pi i h x/a} \quad I \propto |F(h)|^2 \quad (\text{intensity})$$

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Example: Structure Factor for NaCl and CsCl



- NaCl (or KCl):
$$F(hkl) = f_+ [1 + (-1)^{h+k} + (-1)^{h+l} + (-1)^{k+l}] + f_- [(-1)^{h+k+l} + (-1)^h + (-1)^k + (-1)^l]$$

$$= \begin{cases} 4(f_+ + f_-) & (h, k, \text{ and } l \text{ are all even}) \\ 4(f_+ - f_-) & (h, k, \text{ and } l \text{ are all odd}) \\ 0 & (\text{otherwise}) \end{cases} \quad (= 0 \text{ for KCl, why?})$$

- CsCl (or CsBr, CsI):
$$F(hkl) = \begin{cases} f_+ + f_- & (h, k, \text{ and } l \text{ are all or just one even}) \\ f_+ - f_- & (h, k, \text{ and } l \text{ are all or just one odd}) \end{cases}$$

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- Three-dimension (more types of atoms)

$$F(hkl) = \sum_j f_j e^{2\pi i \left(\frac{hx_j}{a} + \frac{ky_j}{b} + \frac{lz_j}{c} \right)} = \sum_j f_j e^{2\pi i (hx'_j + ky'_j + lz'_j)}$$

$$I \propto |F(hkl)|^2 \quad x'_j = x_j/a \quad y'_j = y_j/b \quad z'_j = z_j/c$$

Body-centered cubic unit cell of identical atoms

- Lattice Points: (0,0,0), (1,0,0), (0,1,0), (0,0,1), (1,1,0), (1,0,1), (0,1,1), (1,1,1), (1/2,1/2,1/2)

- Structure factor:

$$\begin{aligned} F(hkl) &= \frac{1}{8} f [e^{2\pi i (0+0+0)} + e^{2\pi i (h+0+0)} + e^{2\pi i (0+k+0)} + e^{2\pi i (0+0+l)} \\ &\quad + e^{2\pi i (h+k+0)} + e^{2\pi i (h+0+l)} + e^{2\pi i (0+k+l)} + e^{2\pi i (h+k+l)}] + f [e^{2\pi i (\frac{h}{2}+\frac{k}{2}+\frac{l}{2})}] \\ &= f [1 + (-1)^{h+k+l}] \quad (0 \text{ if } h+k+l \text{ is an odd number}) \end{aligned}$$

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5. The Structure Factor and the Electron Density Are Related by a Fourier Transform

Fourier Transform for Structure Factor and Electron Density

- Structure factor is defined in terms of the scattering of X-rays from atoms located at each of the positions in the unit cell
- In both atomic and molecular crystals, the electron density is NOT localized at individual points within the unit cell

$$F(hkl) = \int_0^a \int_0^b \int_0^c \rho(x, y, z) \exp \left[2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \right] dx dy dz$$

For a crystal of dimensions A, B, and C along a, b, and c:

$$F(hkl) \propto \int_0^A \int_0^B \int_0^C \rho(x, y, z) \exp \left[2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \right] dx dy dz$$

$\rho(x, y, z) = 0$ (outside the crystal)

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$$\propto \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \rho(x, y, z) \exp \left[2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \right] dx dy dz$$

Related to $\rho(x, y, z)$ by Fourier transform

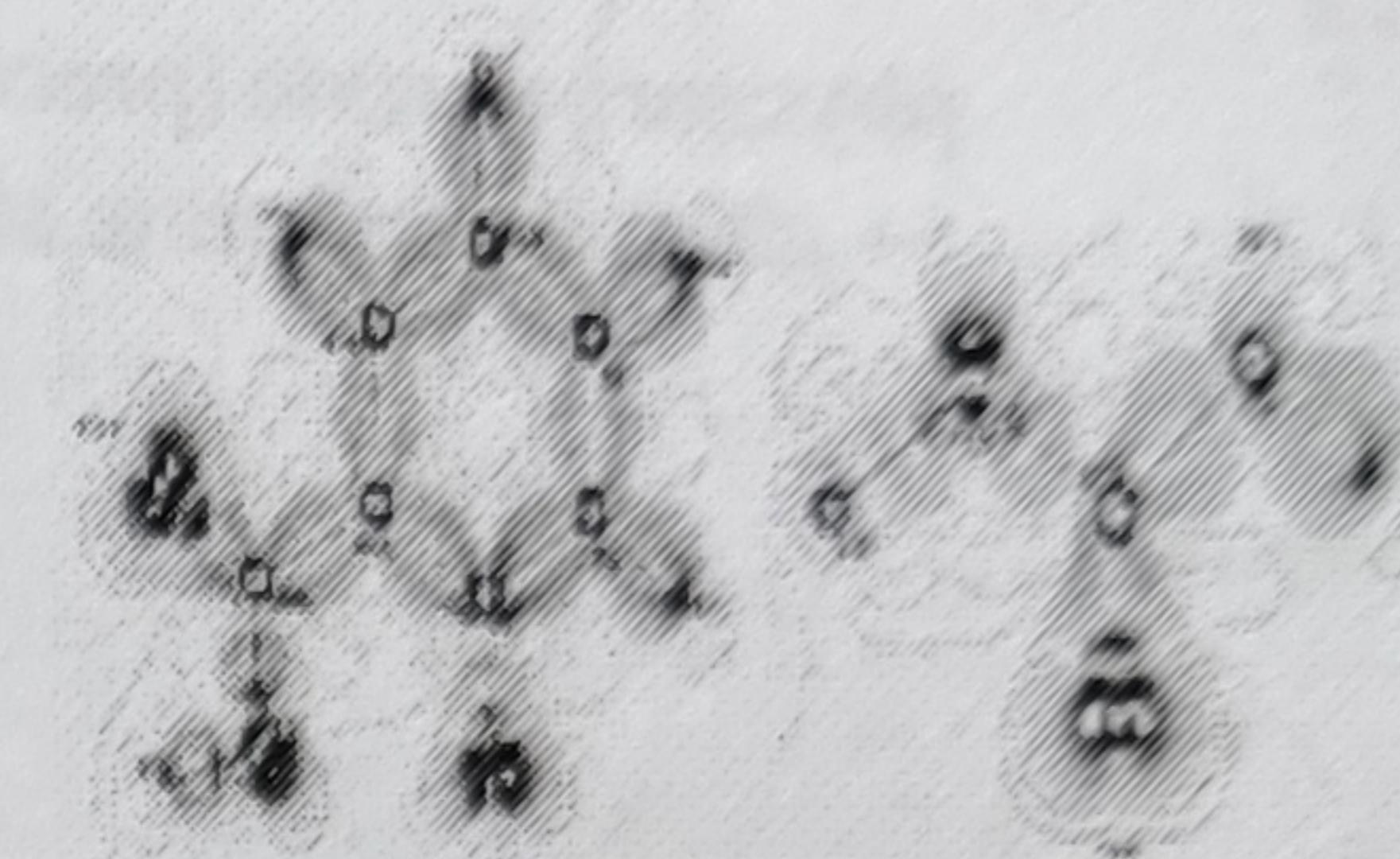
$$\rho(x, y, z) = \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} F(hkl) \exp \left[-2\pi i \left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c} \right) \right]$$

How to Determine Structure Factor F (hkl)?

$$F(hkl) = A(hkl) + iB(hkl)$$

$$I(hkl) \propto |F(hkl)|^2 = [A(hkl)]^2 + [B(hkl)]^2$$

- $|F(hkl)|^2$: given by experimental diffraction patterns
- $A(hkl), B(hkl)$: NOT experimentally determined individually [Phase Problem: how to determine them from $I(hkl)$]



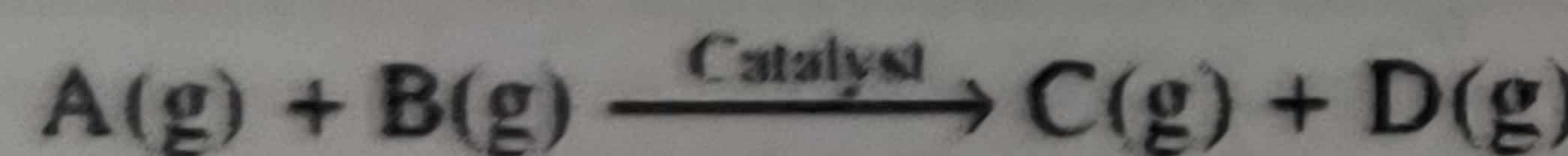
Electron-density map of Aspirin *Cryst. Growth Des.* 12, 4357 (2012).

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6. A Gas Molecule Can Physisorb or Chemisorb to a Solid Surface

The heterogeneous catalysis e.g. gaseous reaction on a solid surface, is explained by this theory as follows:



(i) Diffusion of reactants at the surface of the catalyst.

(ii) Adsorption of reactants at the surface.

Reason: to produce a local reactant concentration much higher than in the gas phase

weak van der Waal's forces (physical adsorption)
partial chemical bonds (chemical adsorption)

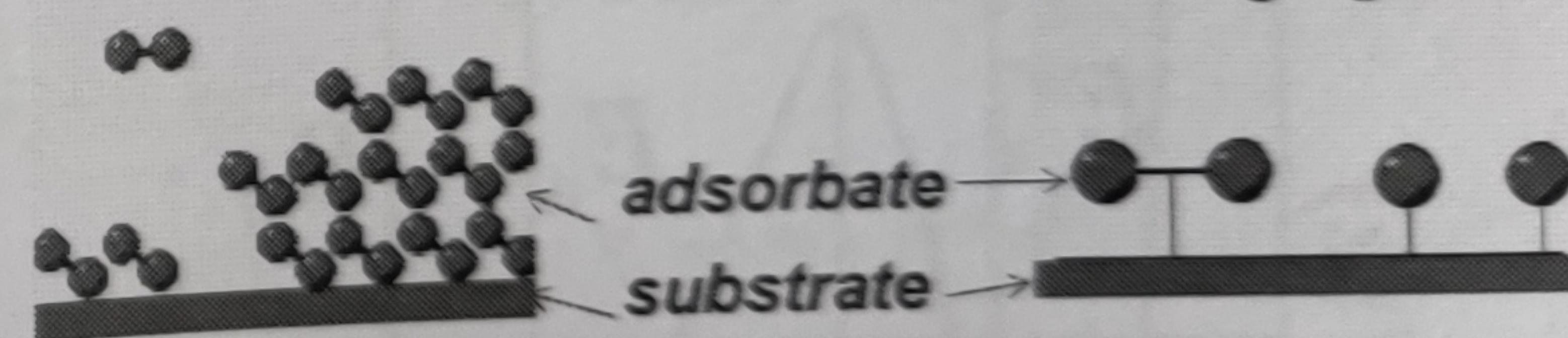
(iii) Reaction of reactants at the surface.

(iv) Desorption of products from the surface.



Adsorption

physisorption



attractive forces:

adsorbate-substrate bond:

bond strength:

van der Waals interactions

long

less than $20 \text{ kJ} \cdot \text{mol}^{-1}$

multilayer

reversible

covalent or ionic for

shorter

$250 \sim 500 \text{ kJ} \cdot \text{mol}^{-1}$

monolayer

irreversible

Adsorption is always an exothermic process, and so $\Delta_{\text{ad}}H < 0$

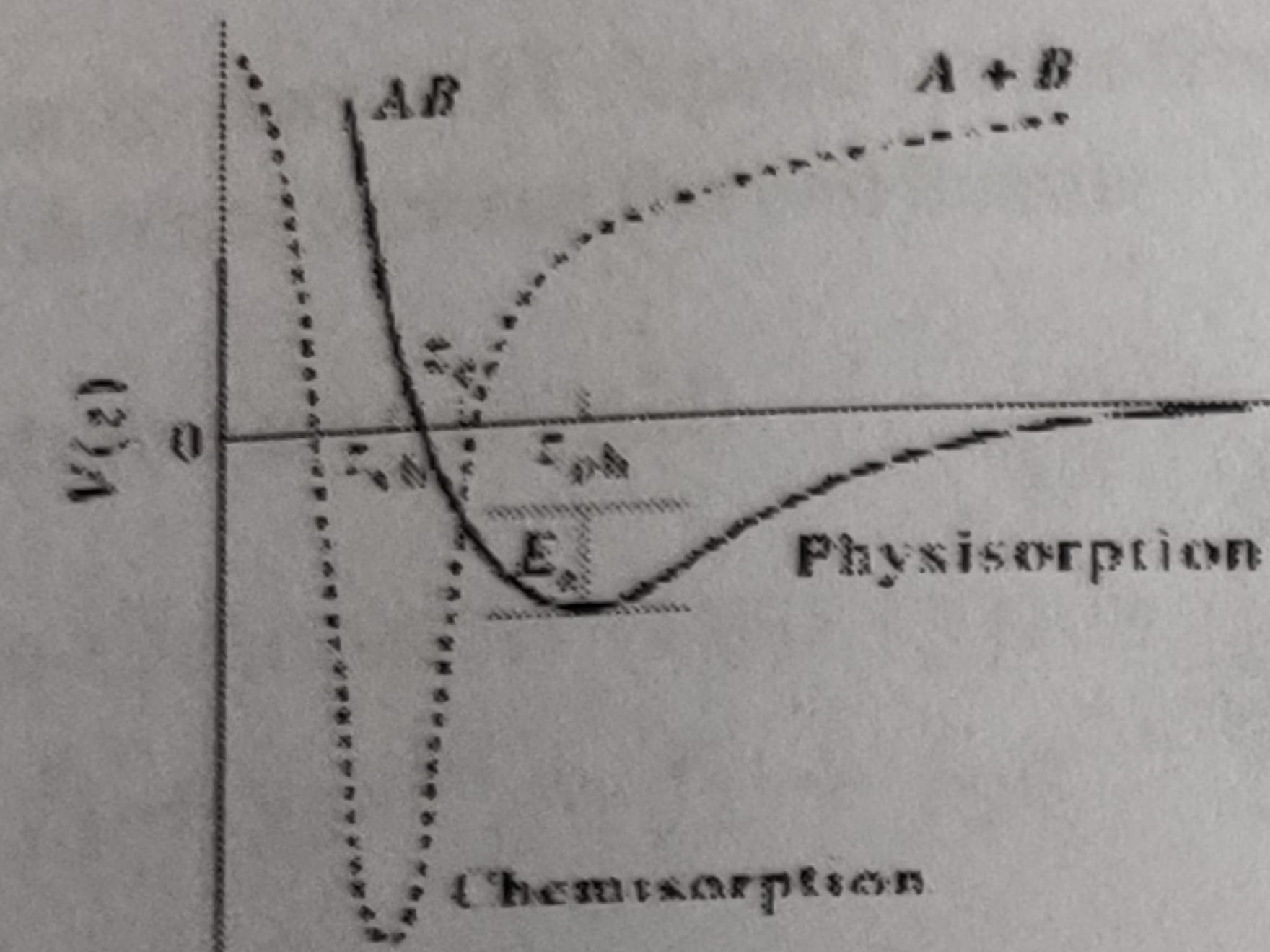
35

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Suppose:

- only one type of binding site
- neither the angle nor the orientation is important
- potential energy depends only on z



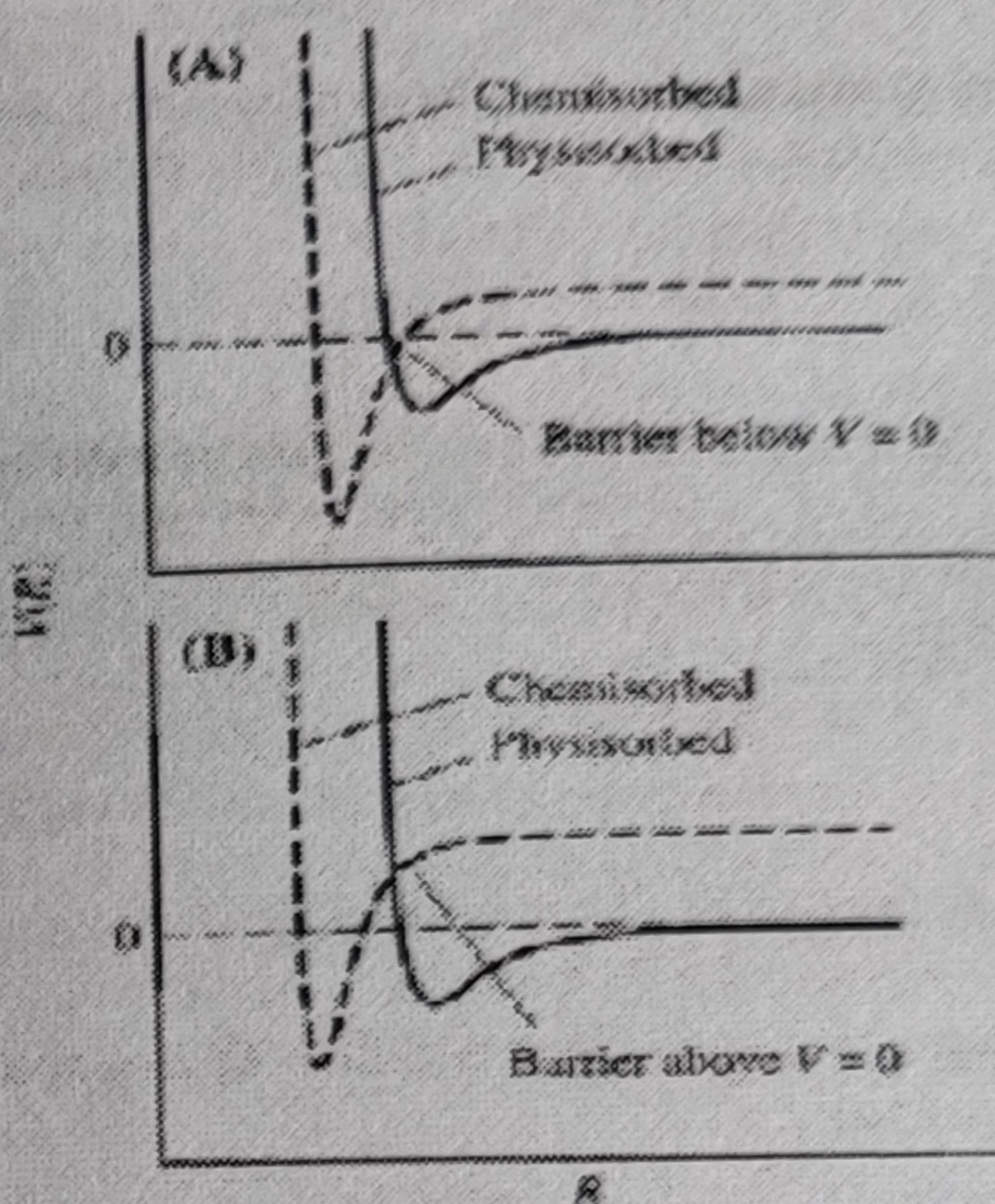
physisorbed state (precursor)
→ chemisorbed state at z_c

One-dimension Simple Model of AB Molecule

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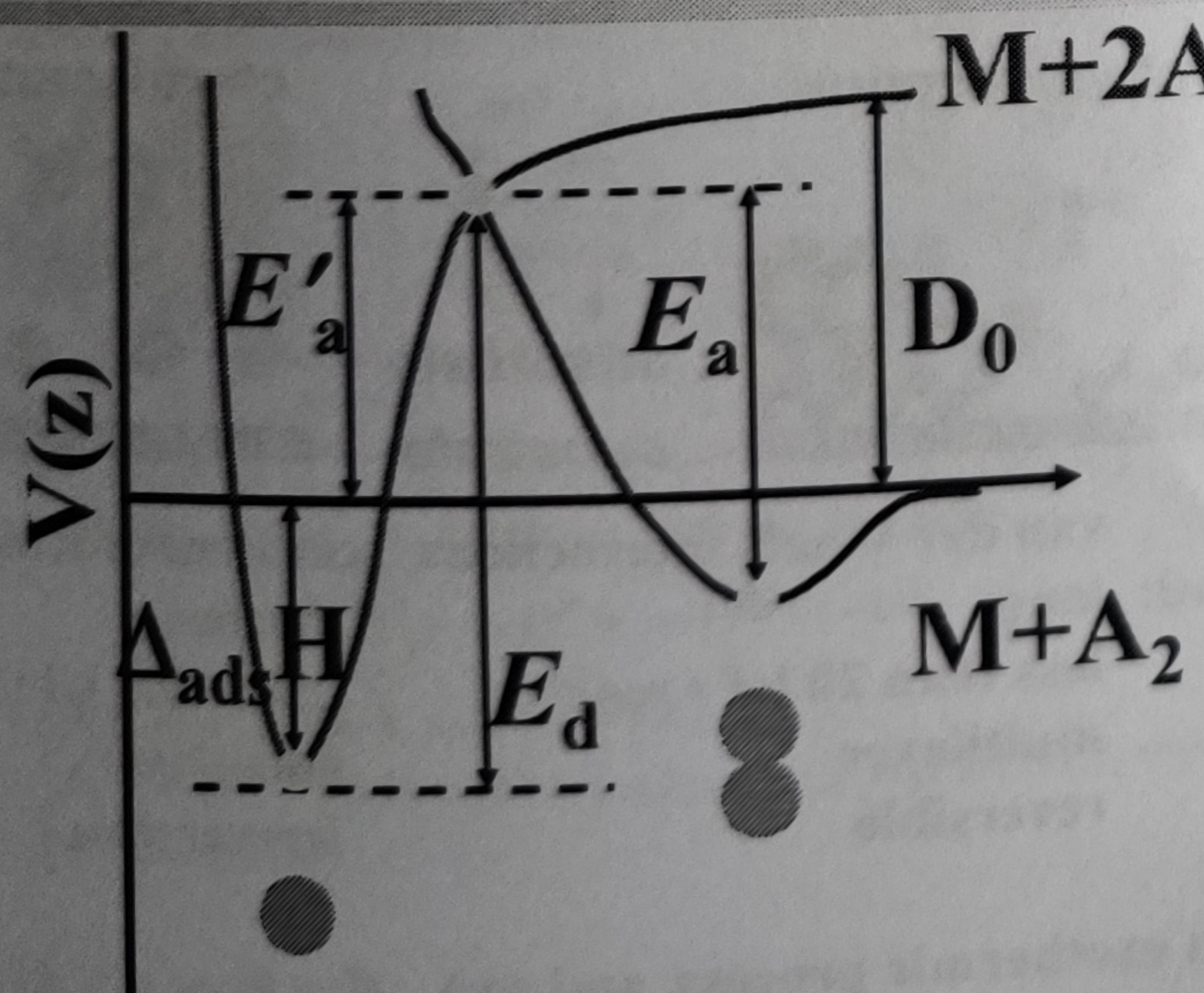


Nonactivated Adsorption (a) and Activated Adsorption (b)



不需活化能的非活化吸附
吸附速度较快

需要活化能的活化吸附
吸附速度较慢



E_a : the activation energy for the conversion from physisorption to chemisorption
 E'_a : the activation energy for chemisorption

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*7. Isotherms Are Plots of Surface Coverage as a Function of Gas Pressure at Constant Temperature

Adsorption Isotherms

— plots of surface coverage as a function of gas pressure at constant temperature

Adsorption isotherm can determine:

- equilibrium constant for the adsorption-desorption reaction
- concentration of surface sites available for adsorption
- enthalpy of adsorption

Langmuir adsorption isotherm (1918) assume:

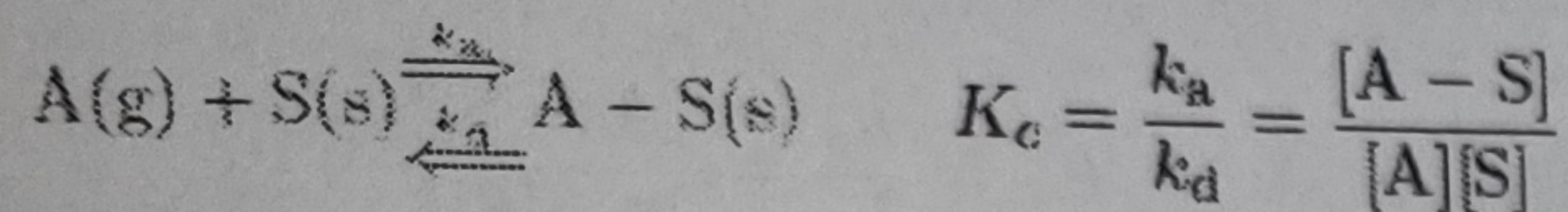
- adsorbed molecules do NOT interact with one another
- enthalpy of adsorption is independent of surface coverage
- finite number of surface sites where molecules can adsorb

I. Langmuir, J. Am. Soc. Chem. 40, 1361 (1918).

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Langmuir Adsorption Isotherms



$$v_a = k_a(1 - \theta)\sigma_0[A] \quad v_d = k_d\theta\sigma_0 \quad \text{rate of adsorption/desorption}$$

- σ_0 : concentration of surface sites (m^{-2})
- θ : fraction of surface sites occupied by an adsorbate
- $\sigma = \theta\sigma_0$: adsorbate concentration on the surface

Adsorption-desorption equilibrium

$$k_d\theta = k_a(1 - \theta)[A] \implies \frac{1}{\theta} = 1 + \frac{1}{K_c[A]}$$

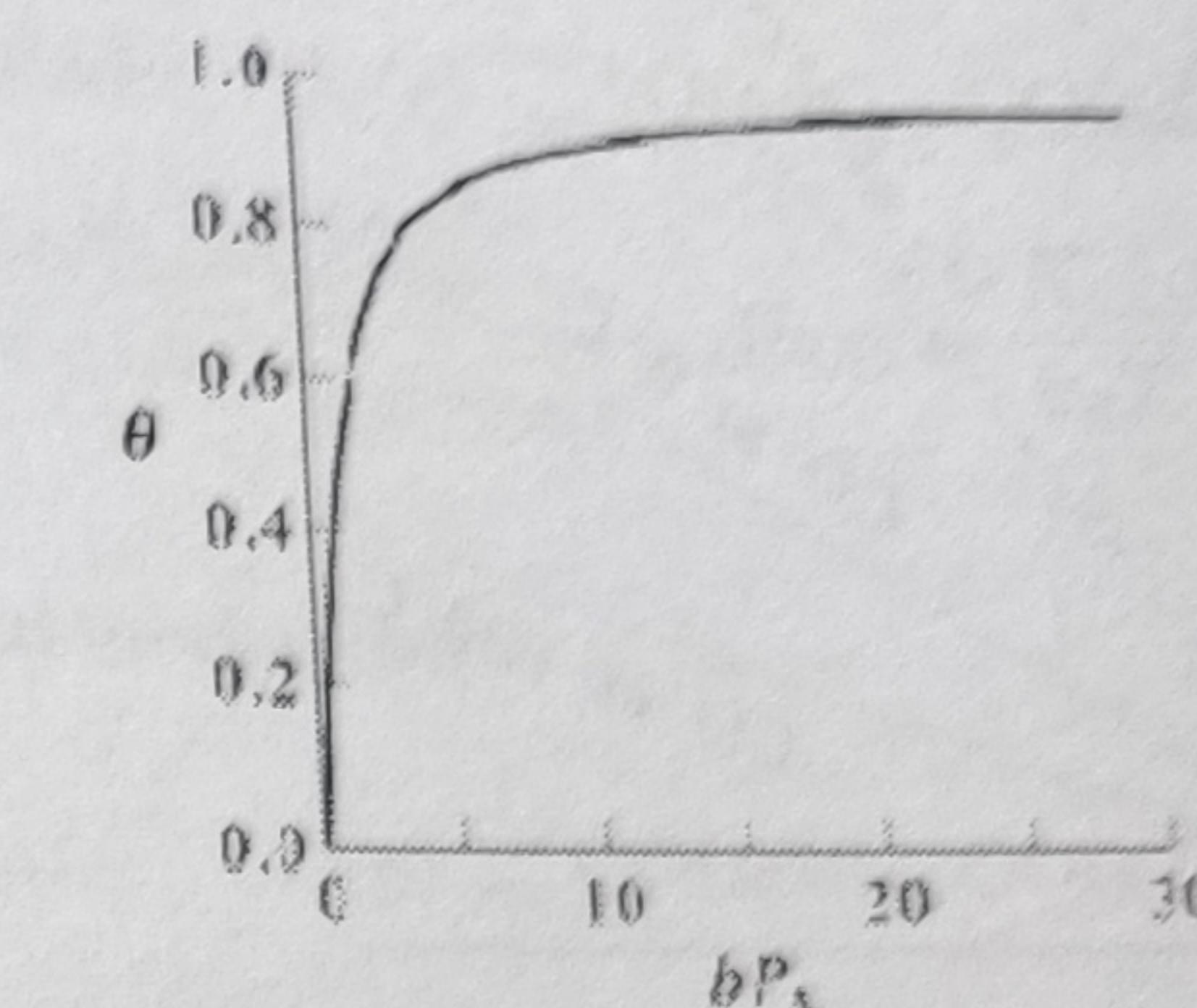
$$\text{or } \frac{1}{\theta} = 1 + \frac{1}{bP_A} \quad (b = \frac{K_c}{k_B T})$$

$$\theta = \frac{bP_A}{1 + bP_A}$$

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Langmuir Adsorption Isotherms



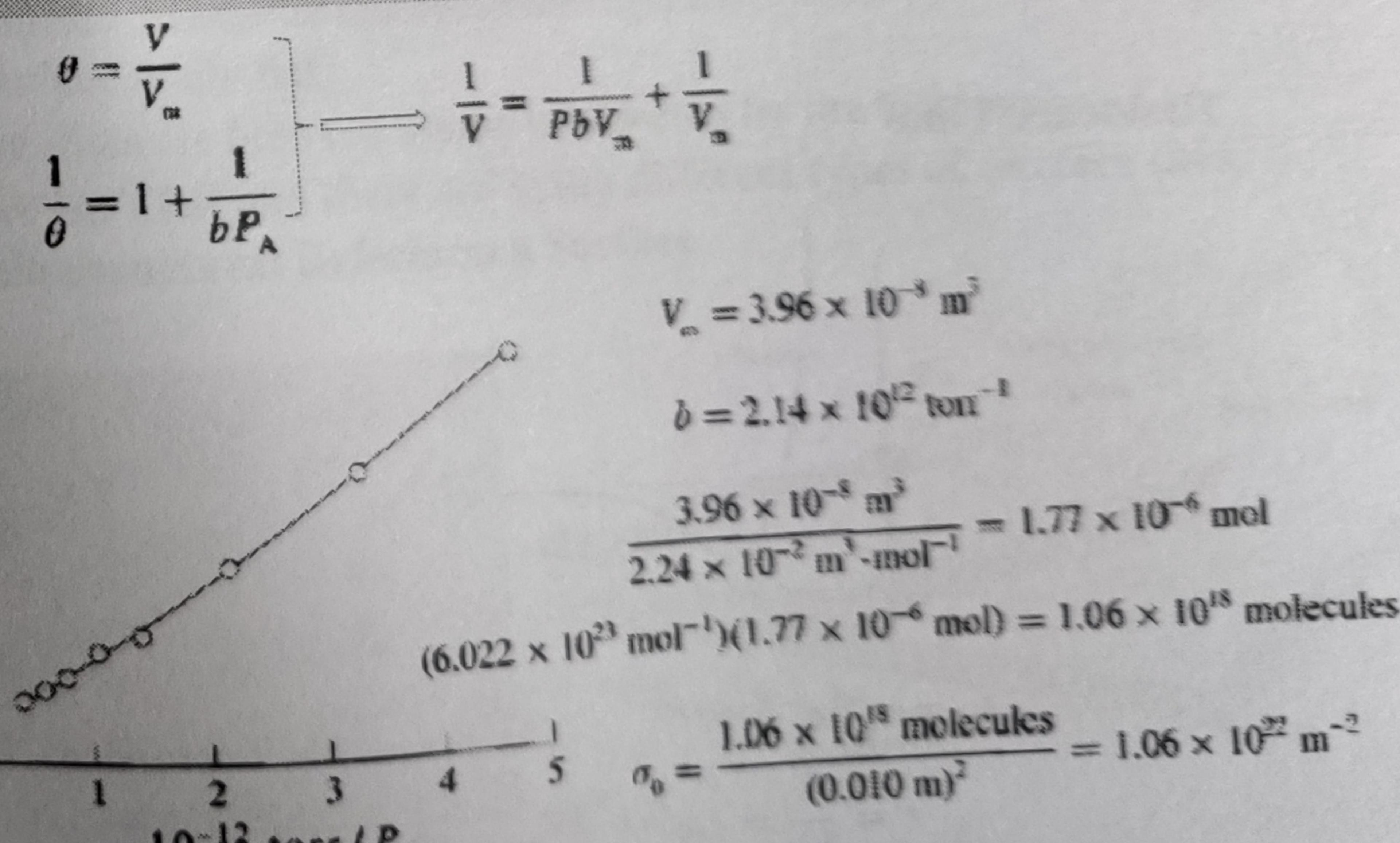
b and total number of surface sites available can be determined

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EXAMPLE 29-10

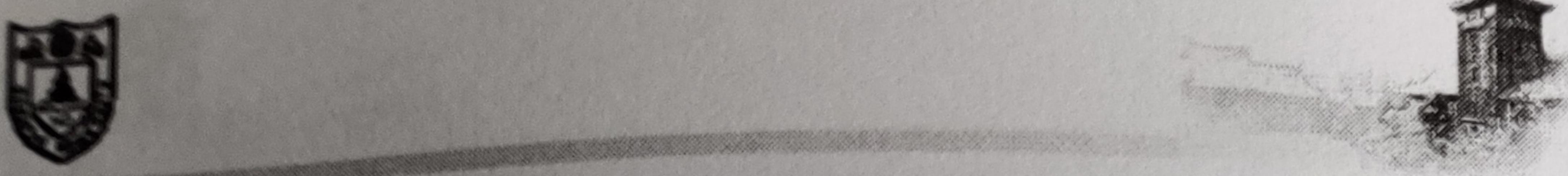
Experimental adsorption data are often tabulated as the equivalent volume of gas, V_e , that will adsorb onto the surface at a particular temperature and pressure. Typically, this volume of adsorbed gas is tabulated as the volume that the gas would occupy under a pressure of one atmosphere at 273.15 K (0°C). Langmuir studied the adsorption of $N_2(g)$ onto a mica surface at 273.15 K. From the data presented below, determine the values of b and V_e , the volume of gas that corresponds to a monolayer coverage. Use this value of V_e to determine the total number of surface sites.

$P/10^{-12}$ torr	$V/10^{-8}$ m ³
2.55	3.39
1.79	3.17
1.30	2.89
0.98	2.62
0.71	2.45
0.46	1.95
0.30	1.55
0.21	1.23



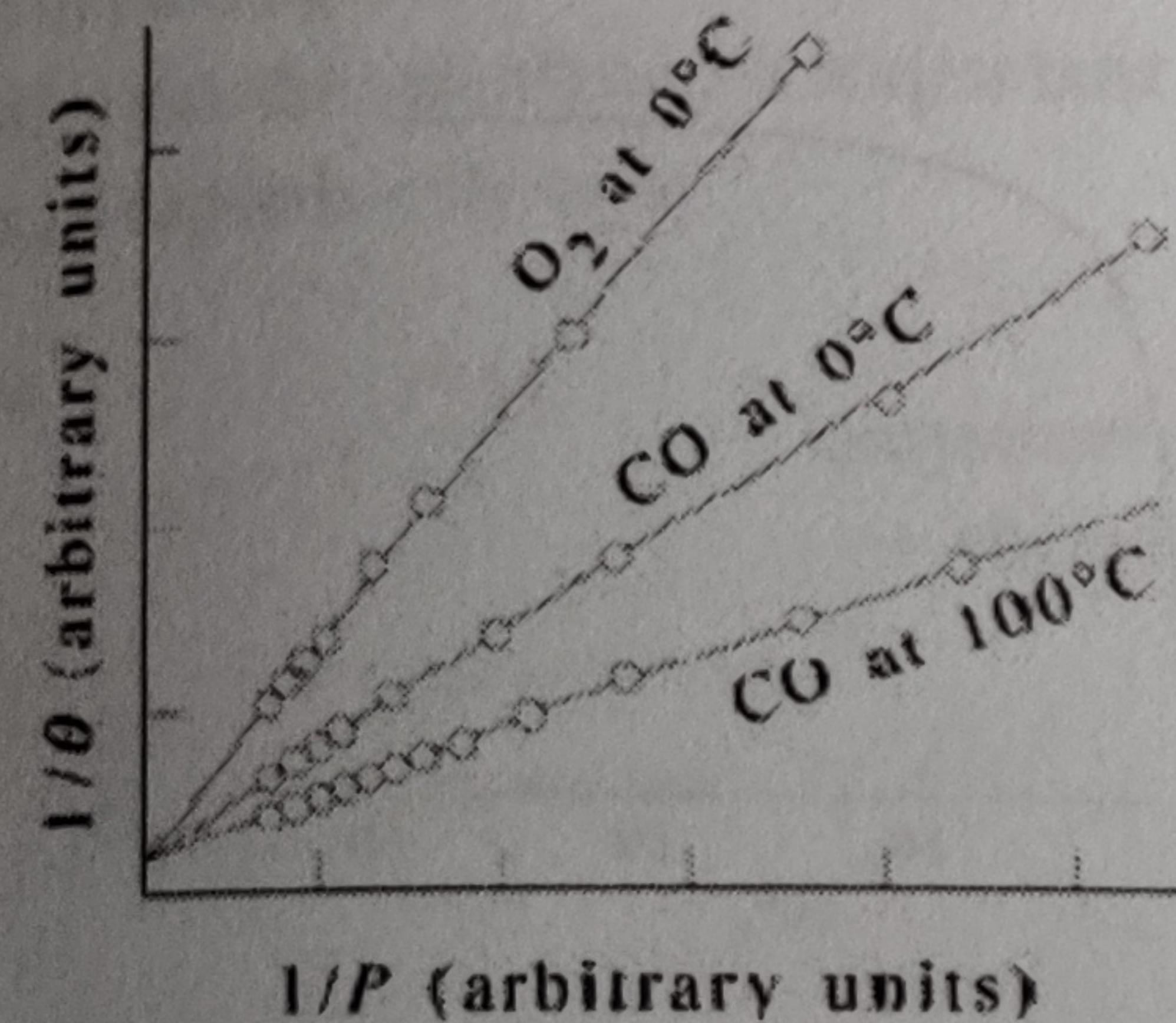
43

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Langmuir Adsorption Isotherms: Diatomic Dissociation

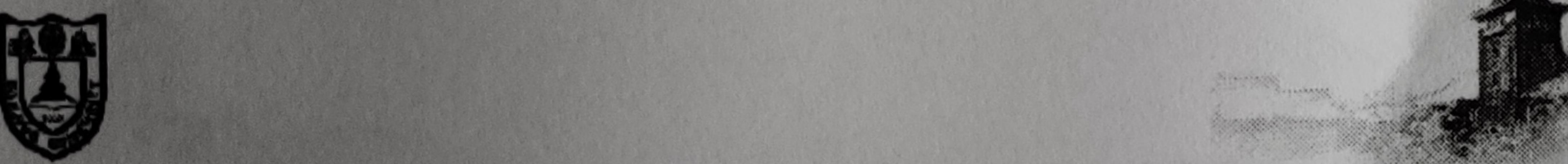
Langmuir Adsorption Isotherms: O and CO on a Si surface



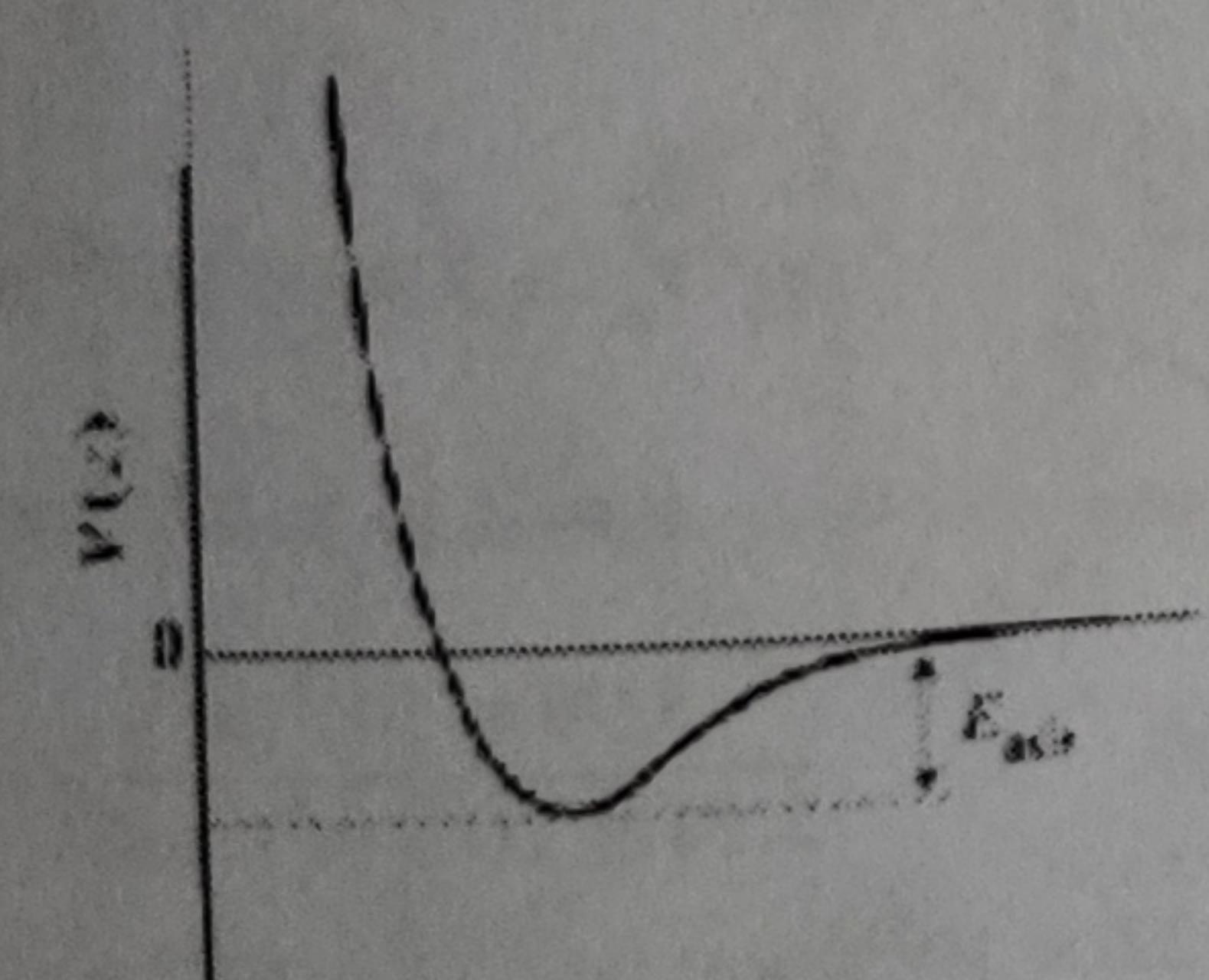
Expl. data are well described by Langmuir adsorption isotherm

45

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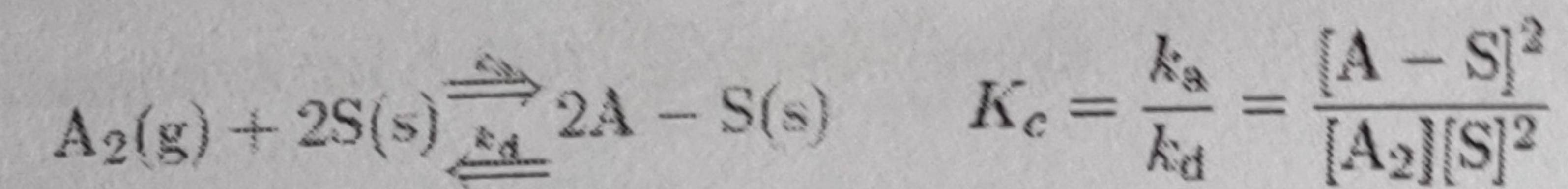
Residence Time



$$k_d = \tau_0^{-1} e^{-E_{\text{ads}}/RT} \quad (\text{Arrhenius-like expression})$$

$$\tau = \frac{1}{k_d} = \tau_0 e^{E_{\text{ads}}/RT} \quad (\text{Residence time})$$

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$$v_a = k_a(1 - \theta)^2 \sigma_0^2 [A_2] \quad v_d = k_d \theta^2 \sigma_0^2$$

Adsorption-desorption equilibrium

$$k_a(1 - \theta)^2 [A_2] = k_d \theta^2 \implies \frac{1}{\theta} = 1 + \frac{1}{K_c^{1/2} [A_2]^{1/2}}$$

$$\text{or } \frac{1}{\theta} = 1 + \frac{1}{b_{A_2}^{1/2} P_{A_2}^{1/2}} \quad (b_{A_2} = \frac{K_c}{k_B T})$$



EXAMPLE 29-12

The enthalpy of adsorption of CO on palladium is $-146 \text{ kJ}\cdot\text{mol}^{-1}$. Estimate the residence time of a CO molecule on a palladium surface at 300 K and 500 K. (Assume that $\tau_0 = 1.0 \times 10^{-12} \text{ s}$.)

SOLUTION: The residence time is given by Equation 29.38

$$\tau = \tau_0 e^{E_{\text{ads}}/RT}$$

At $T = 300 \text{ K}$

$$\tau = (1.0 \times 10^{-12} \text{ s}) \exp \left\{ \frac{-146 \times 10^3 \text{ J}\cdot\text{mol}^{-1}}{(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(300 \text{ K})} \right\} \\ = 2.6 \times 10^{13} \text{ s}$$

and at $T = 500 \text{ K}$

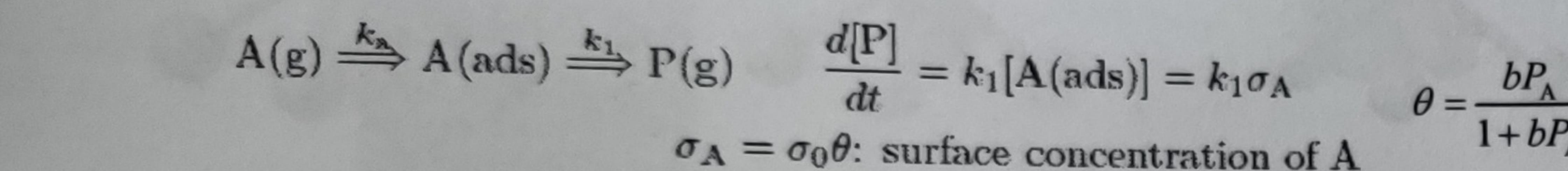
$$\tau = (1.0 \times 10^{-12} \text{ s}) \exp \left\{ \frac{-146 \times 10^3 \text{ J}\cdot\text{mol}^{-1}}{(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(500 \text{ K})} \right\} \\ = 1800 \text{ s}$$

Notice that the residence time is very temperature sensitive.

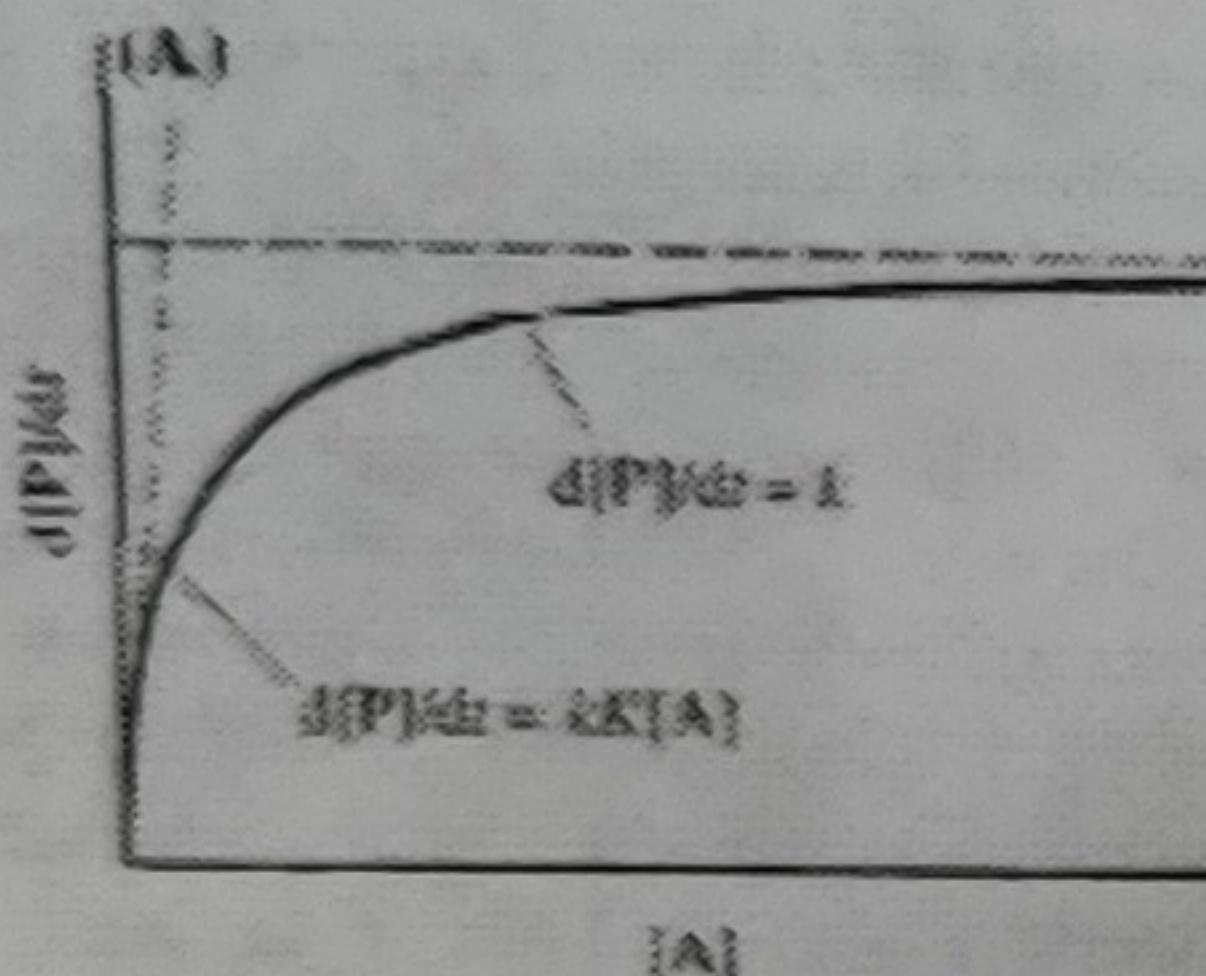
*8. The Langmuir Adsorption Isotherm Can Be Used to Derive Rate Laws for Surface-Catalyzed Gas-Phase Reactions

Unimolecular Surface Gas-phase Reactions

- Two-step mechanism



$$v = \frac{d[P]}{dt} = k_1 \frac{\sigma_0 K_c [A]}{1+K_c[A]} = k_1 \frac{\sigma_0 b P_A}{1+bP_A} \quad (b = \frac{K_c}{k_B T}) = \begin{cases} k_1 \sigma_0 b P_A = k_{\text{obs}} P_A & (\text{low gas pressure}) \\ k_1 \sigma_0 = k_{\text{obs}} & (\text{high gas pressure}) \end{cases}$$



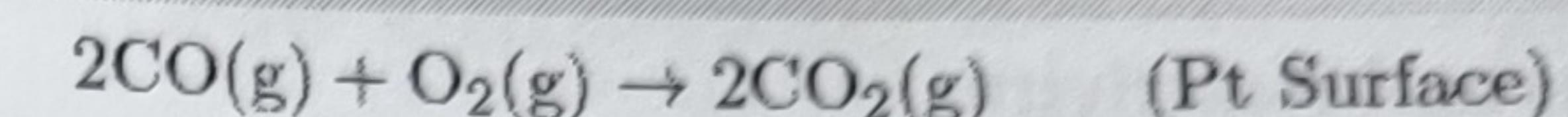
The rate should approach an upper limit as the pressure increases

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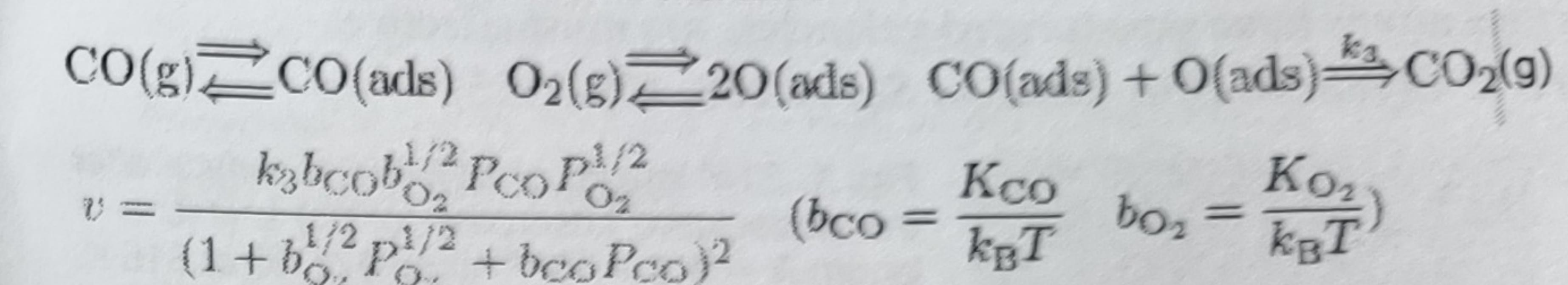
50



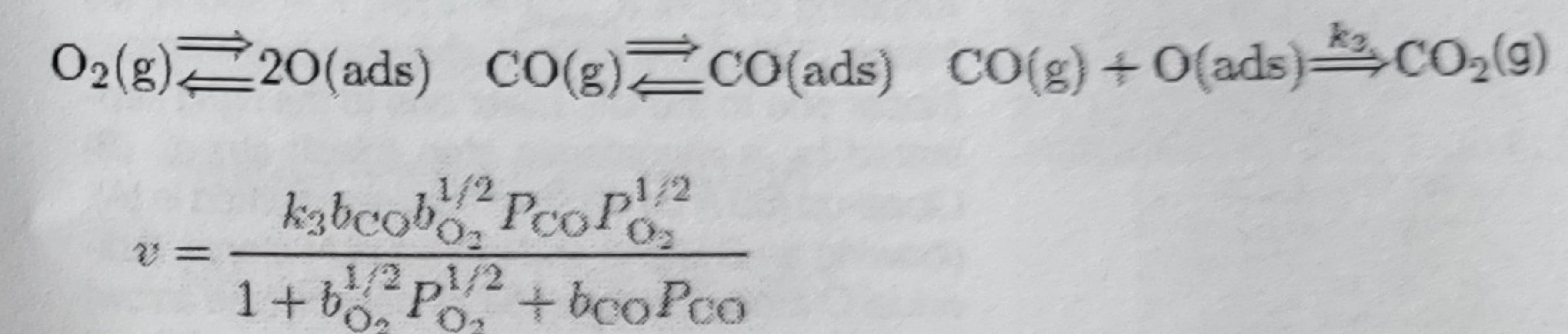
Bimolecular Surface Gas-phase Reactions



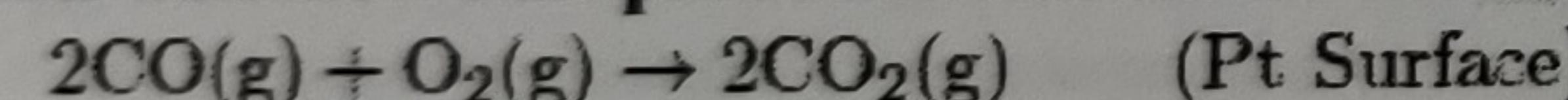
- Langmuir-Hinshelwood mechanism



- Eley-Rideal mechanism

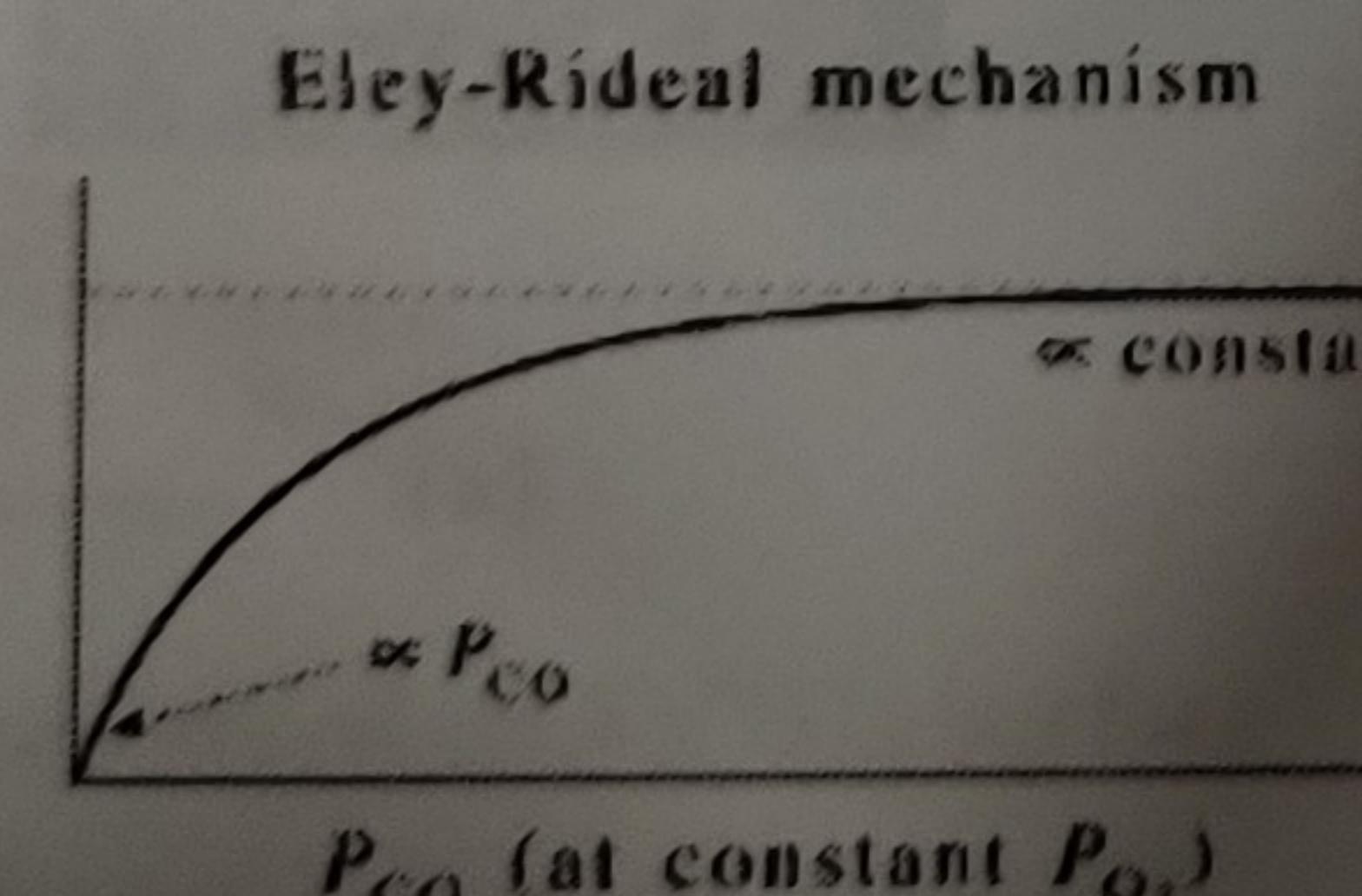
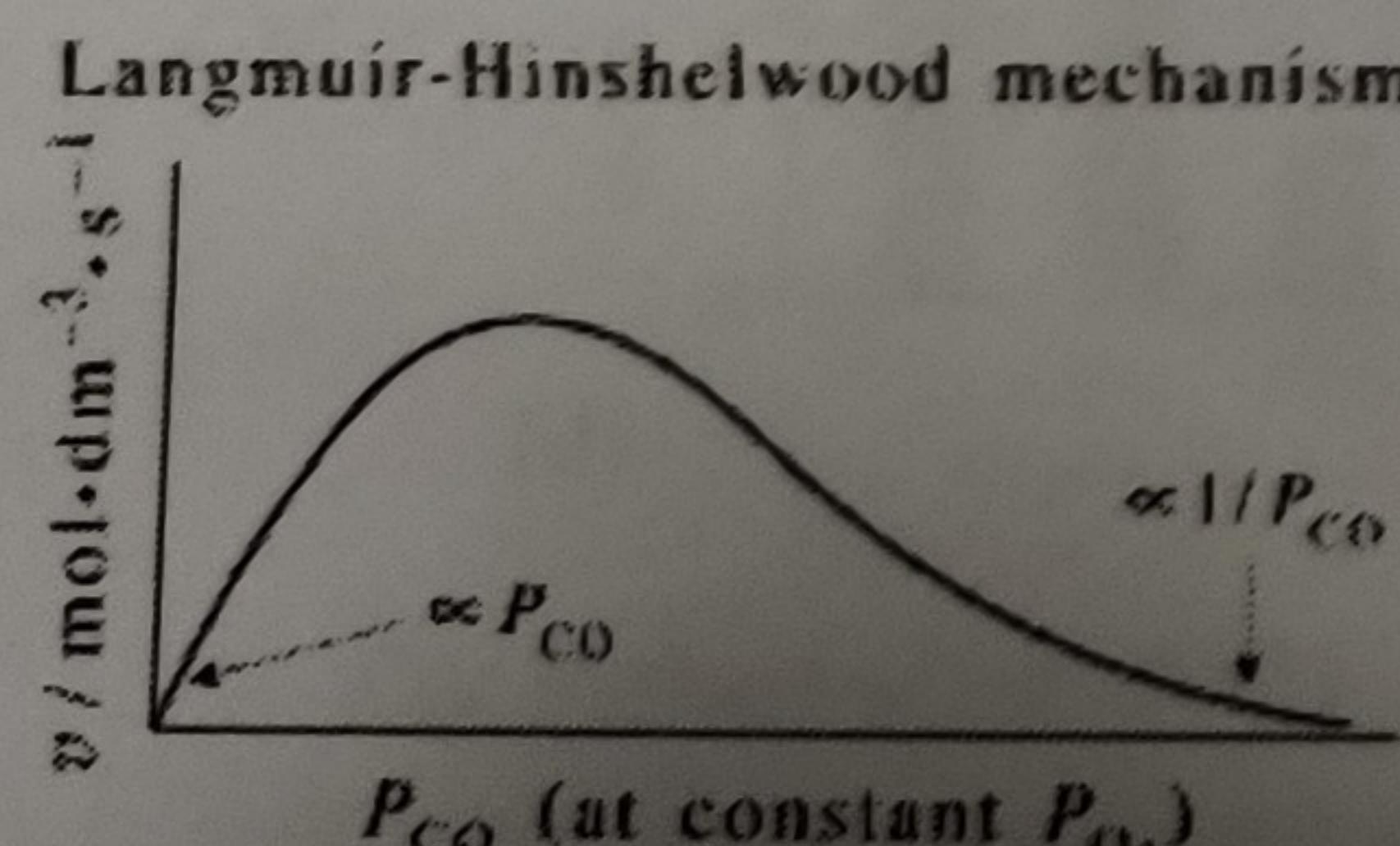


Bimolecular Surface Gas-phase Reactions: Behavior



Rate law as a function of P_{CO} at a fixed P_{O_2}

P_{CO}	Langmuir-Hinshelwood	Eley-Rideal mechanism
$\ll P_{\text{O}_2}$	$v \approx \frac{k_3 b_{\text{CO}} b_{\text{O}_2}^{1/2} P_{\text{CO}} P_{\text{O}_2}^{1/2}}{1 + b_{\text{O}_2}^{1/2} P_{\text{O}_2}^{1/2}} \propto P_{\text{CO}}$	$v \approx \frac{k_3 b_{\text{CO}} b_{\text{O}_2}^{1/2} P_{\text{CO}} P_{\text{O}_2}^{1/2}}{(1 + b_{\text{O}_2}^{1/2} P_{\text{O}_2}^{1/2})^2} \propto P_{\text{CO}}$
$\gg P_{\text{O}_2}$	$v \approx \frac{k_3 b_{\text{CO}} b_{\text{O}_2}^{1/2} P_{\text{CO}} P_{\text{O}_2}^{1/2}}{(1 + b_{\text{CO}} P_{\text{CO}})^2} \propto \frac{1}{P_{\text{CO}}}$	$v \approx \frac{k_3 b_{\text{CO}} b_{\text{O}_2}^{1/2} P_{\text{CO}} P_{\text{O}_2}^{1/2}}{1 + b_{\text{CO}} P_{\text{CO}}} \approx \text{constant}$



9. The Structure of a Surface Is Different from that of a Bulk Solid

Are surfaces really flat?

Are the distances between atoms unaffected by the location?

Surface isn't flat and there are many different types of surface sites.

Possible Structural Defects on a Surface

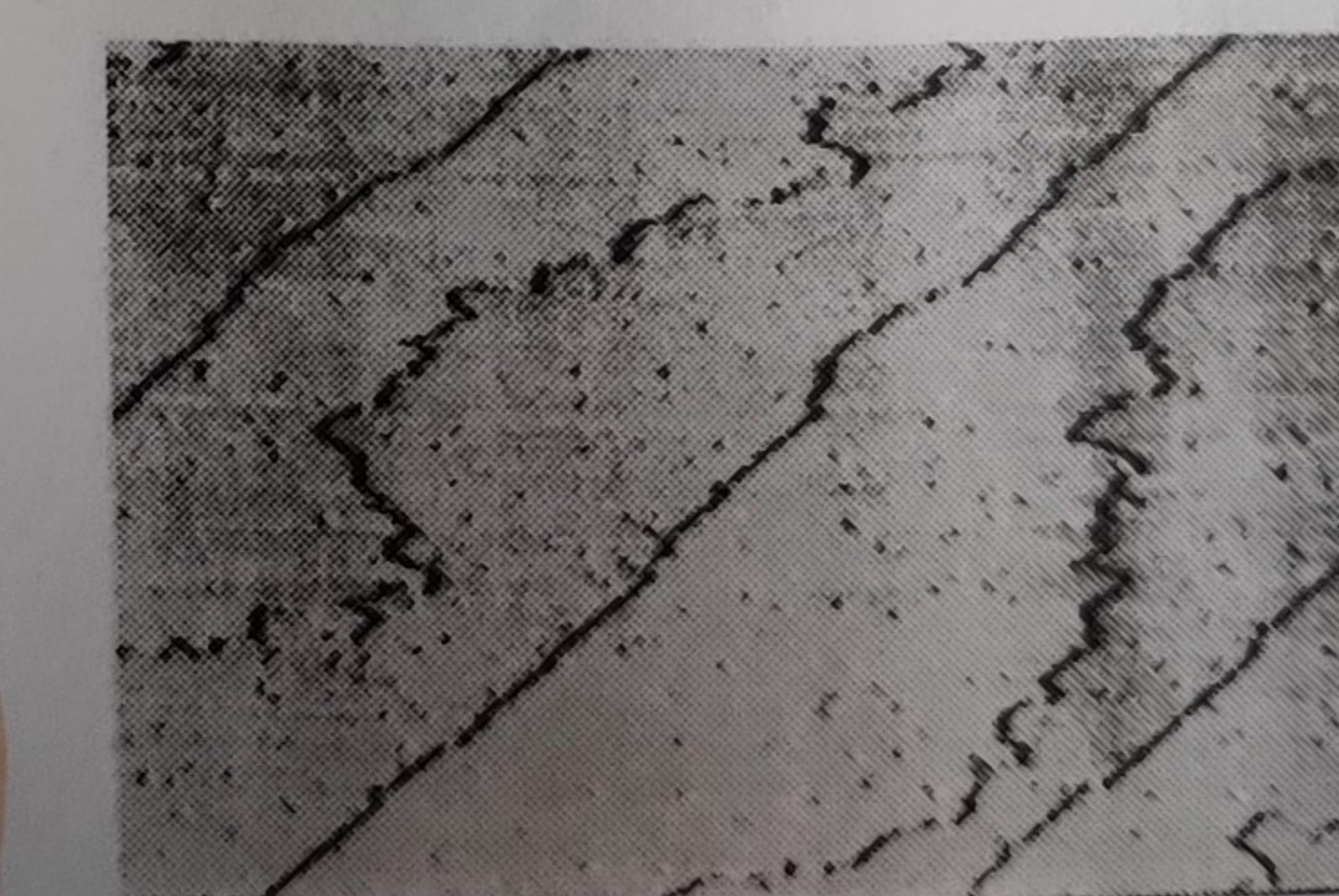
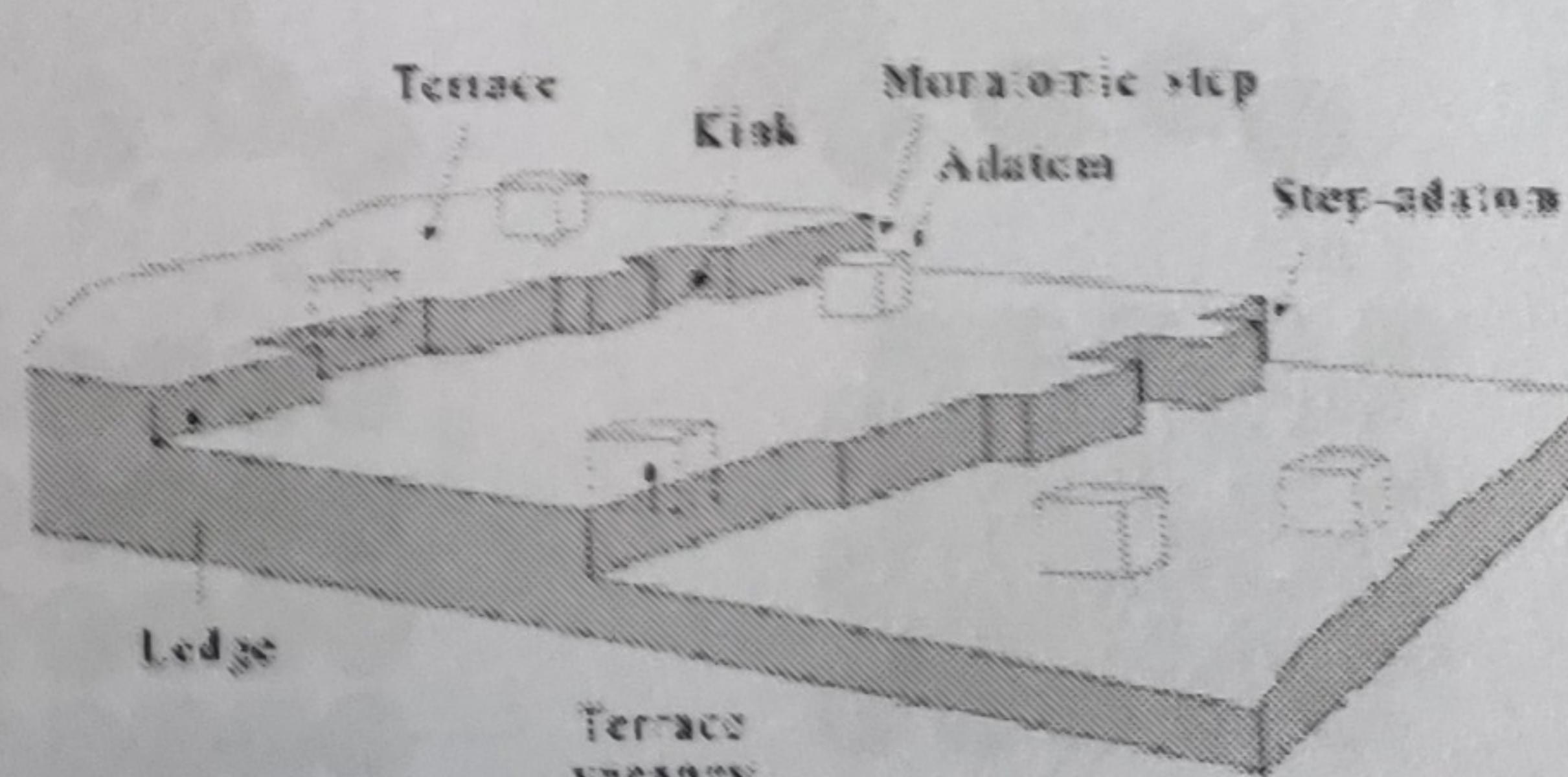


FIG. 1. A 1200-Å STM derivative-mode image of a Si(001) surface miscut 0.3° towards {100}. The surface steps down from left to right.

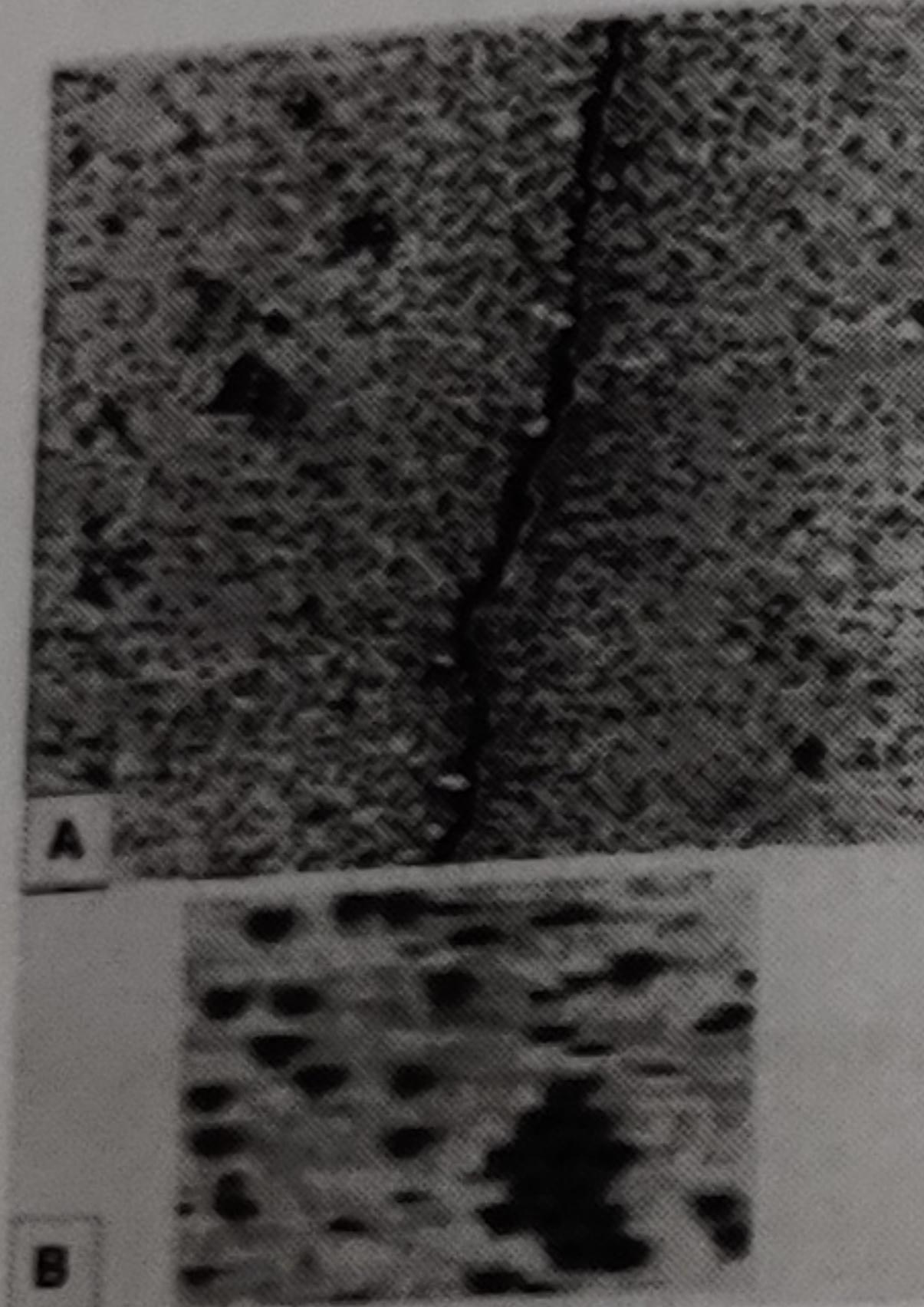




Structural Defects and Reactivity

- The defect sites (step, kink, adatoms, ...), where low-coordinated surface atoms have unsaturated valencies, are most effective.

H. S. Taylor, *R. Soc. London Ser A* 103, 105 (1923).



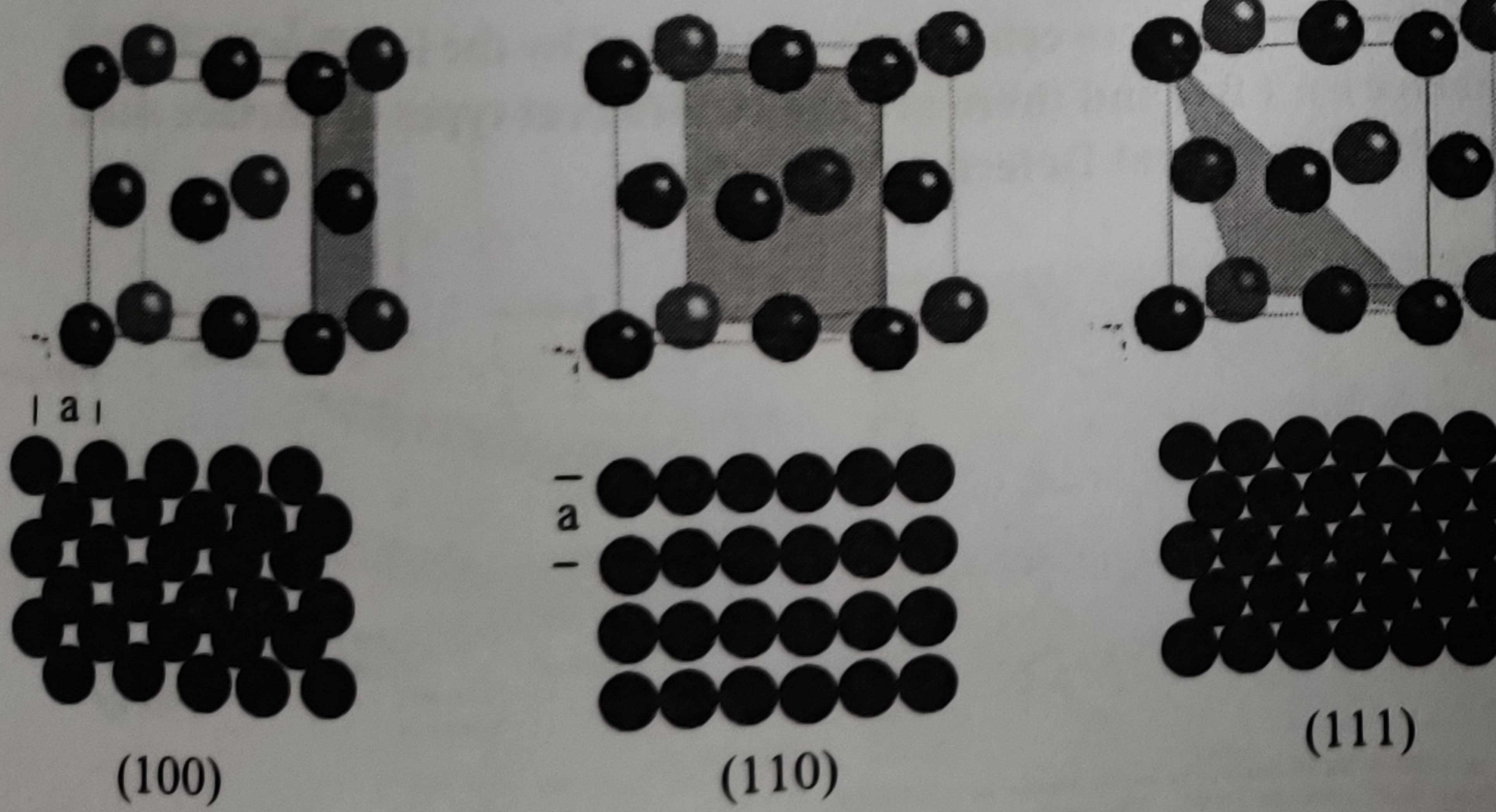
Dissociative Adsorption of NO at 315K on Ru(0001) surface (STM)

5

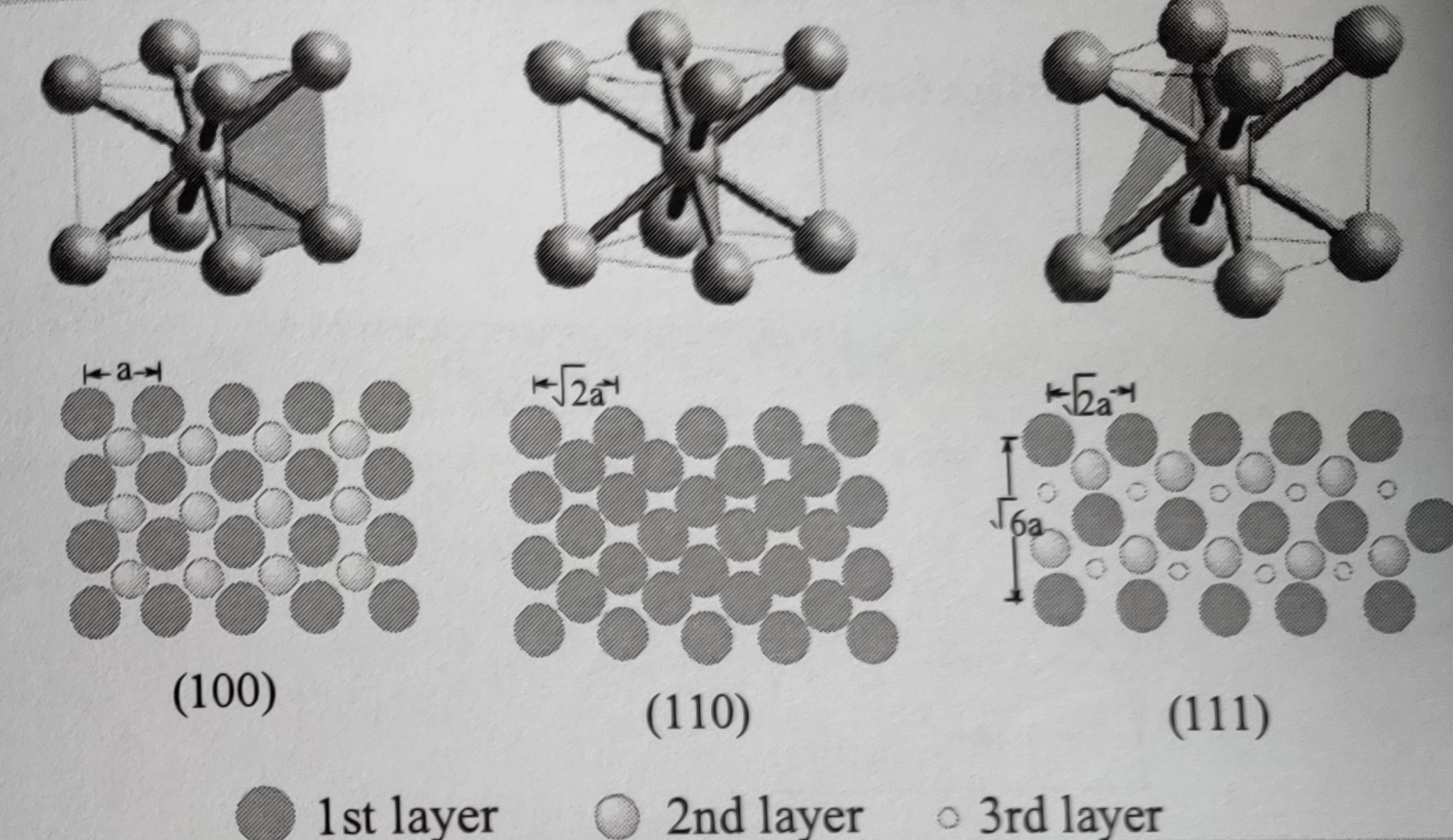
Science 273, 1688 (1996).



(2) fcc (Pt, Au, Cu, ...)



bcc (Fe, W, ...)



○ 1st layer

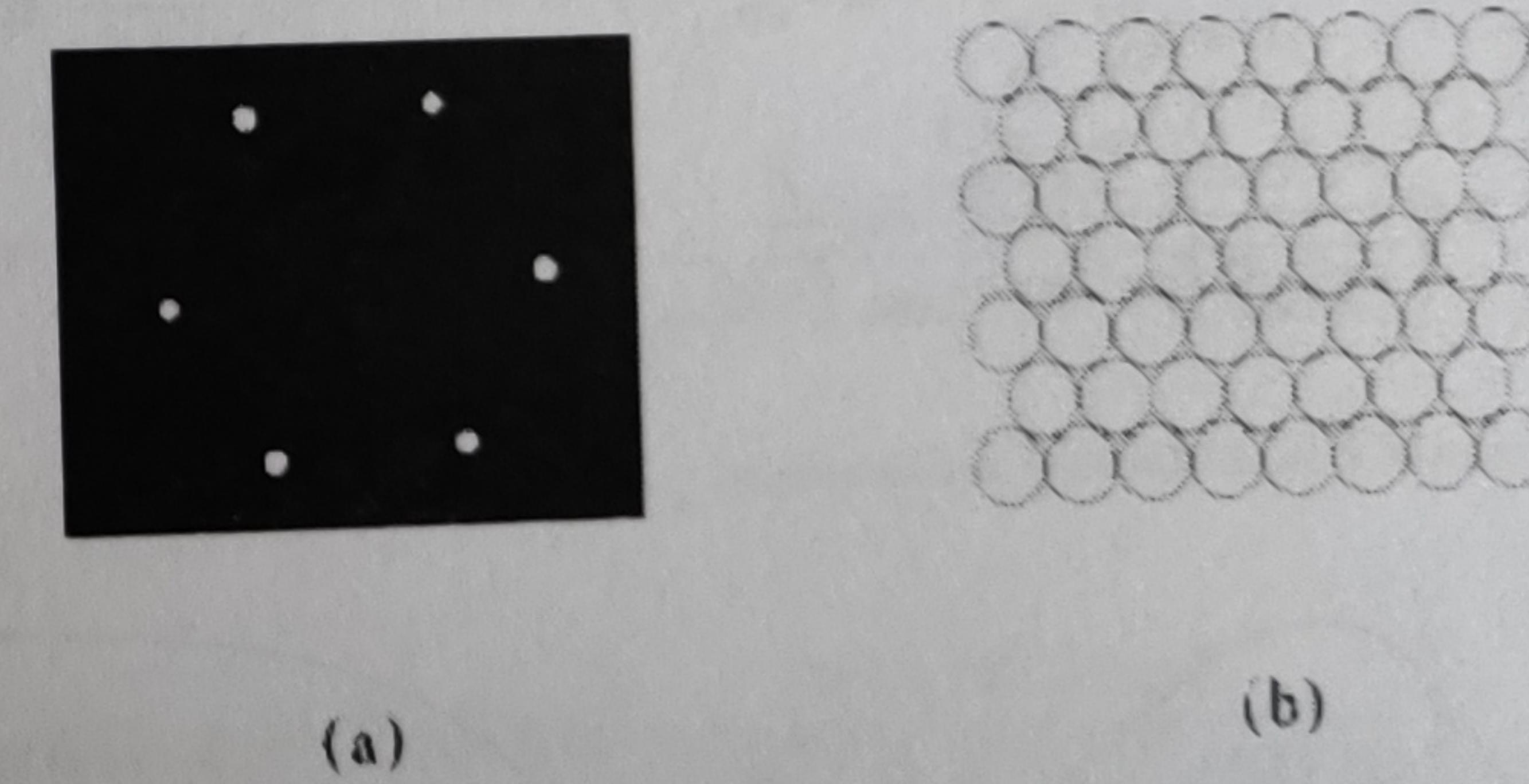
○ 2nd layer

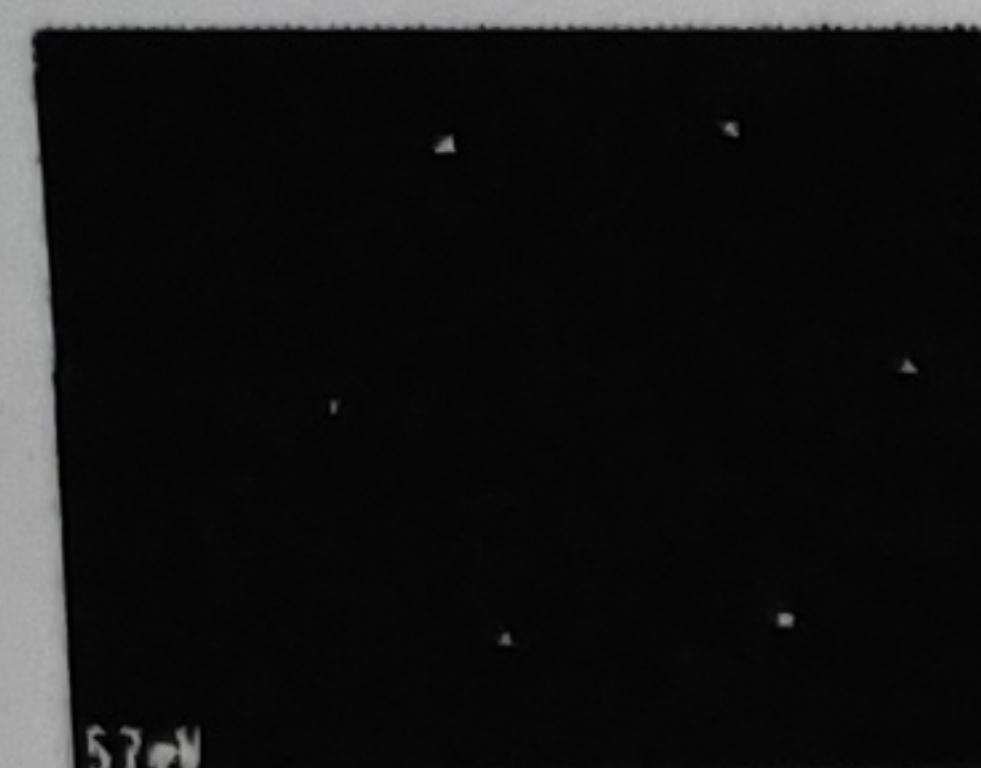
- 3rd layer



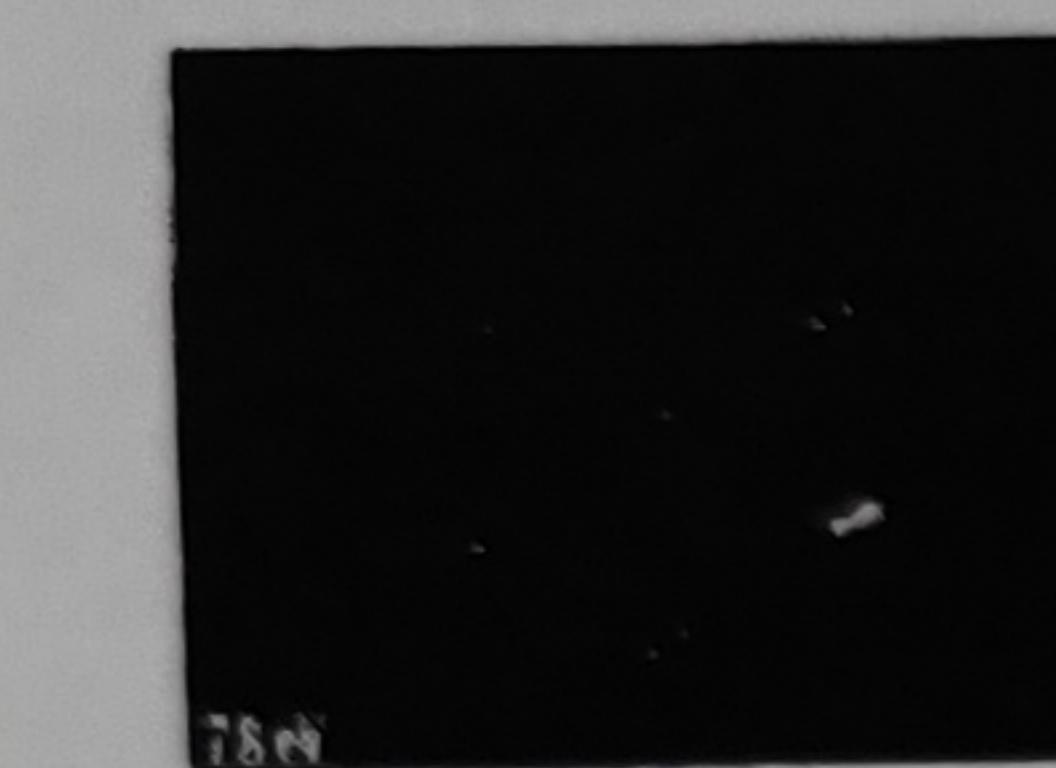
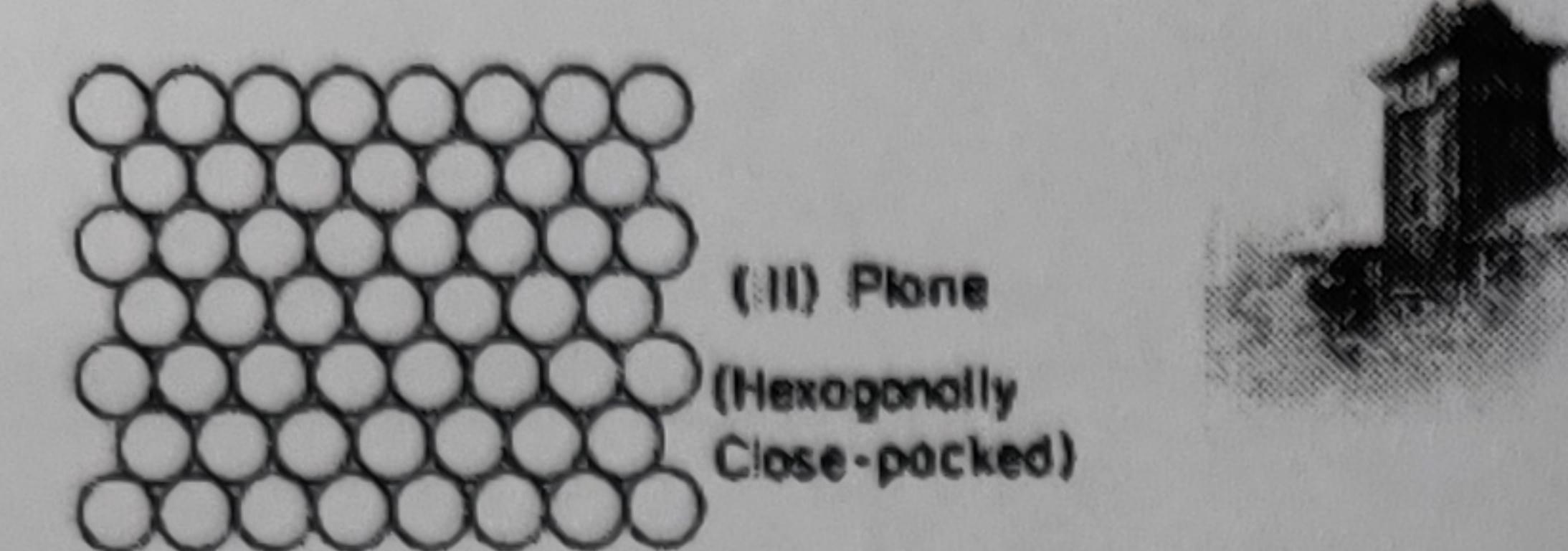
Structure of a Surface Depends on How the Crystal Cut

A Leed (low-energy electron diffraction spectroscopy) Pattern for the 111 Surface of Platinum

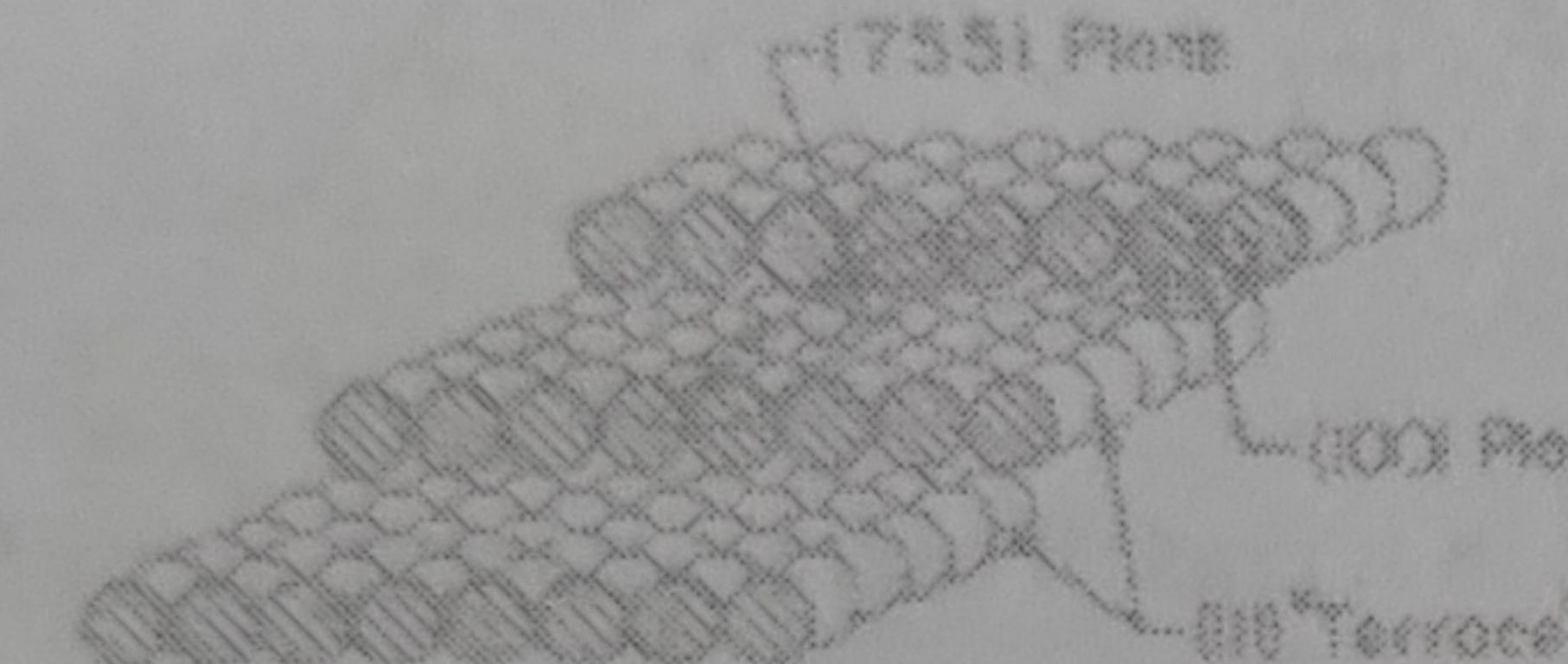




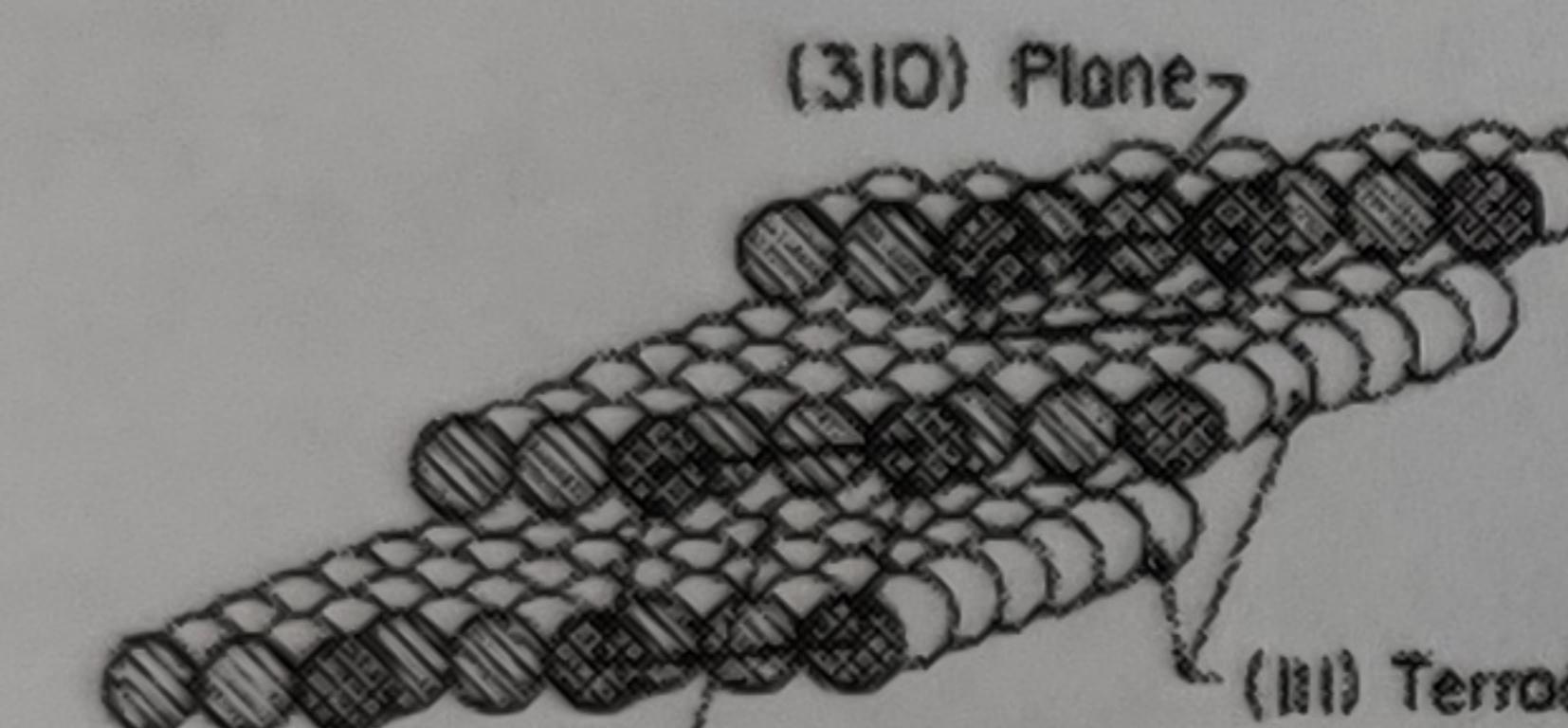
A Pt (III)



B. Pt (S)-[6 (III)x(100)]>>Pt (755)



C. Pt (S)-[7 (III)x(310)]>>Pt (10,8,7)

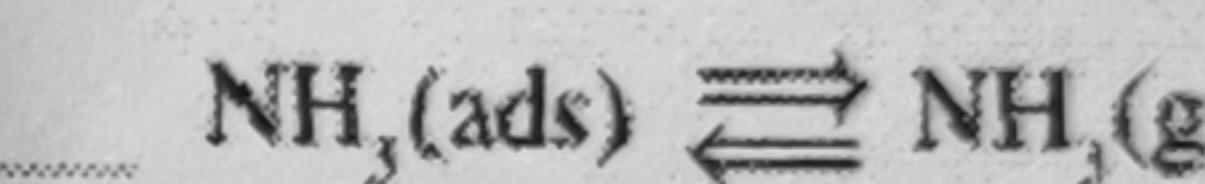
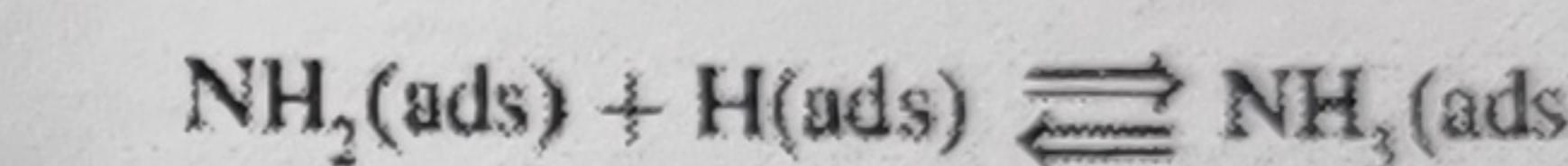
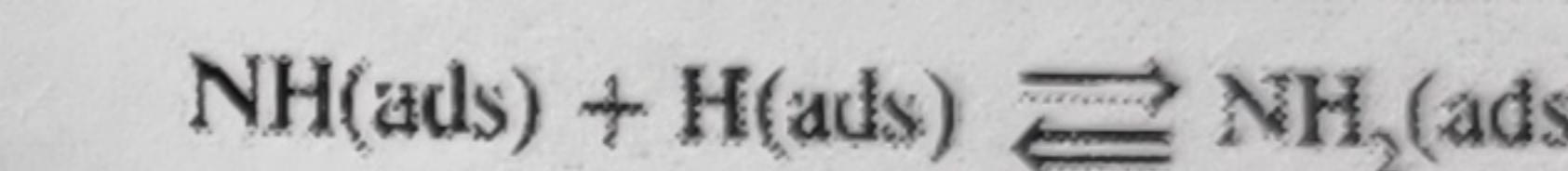
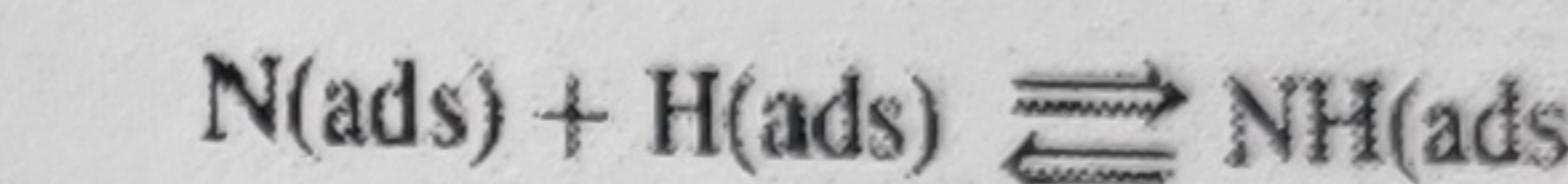
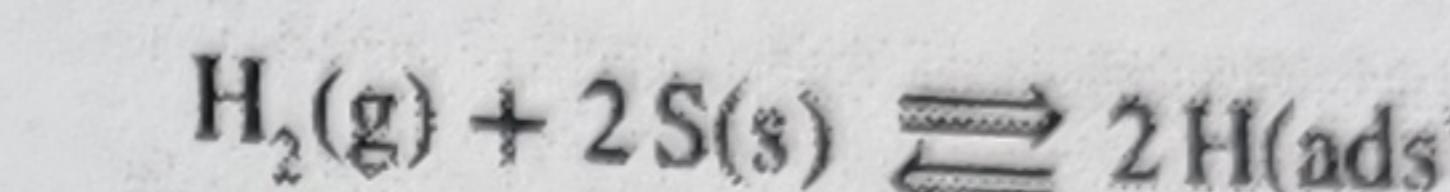


10. The Reaction Between H₂(g) and N₂(g) to Produce NH₃(g) Can Be Surface Catalyzed

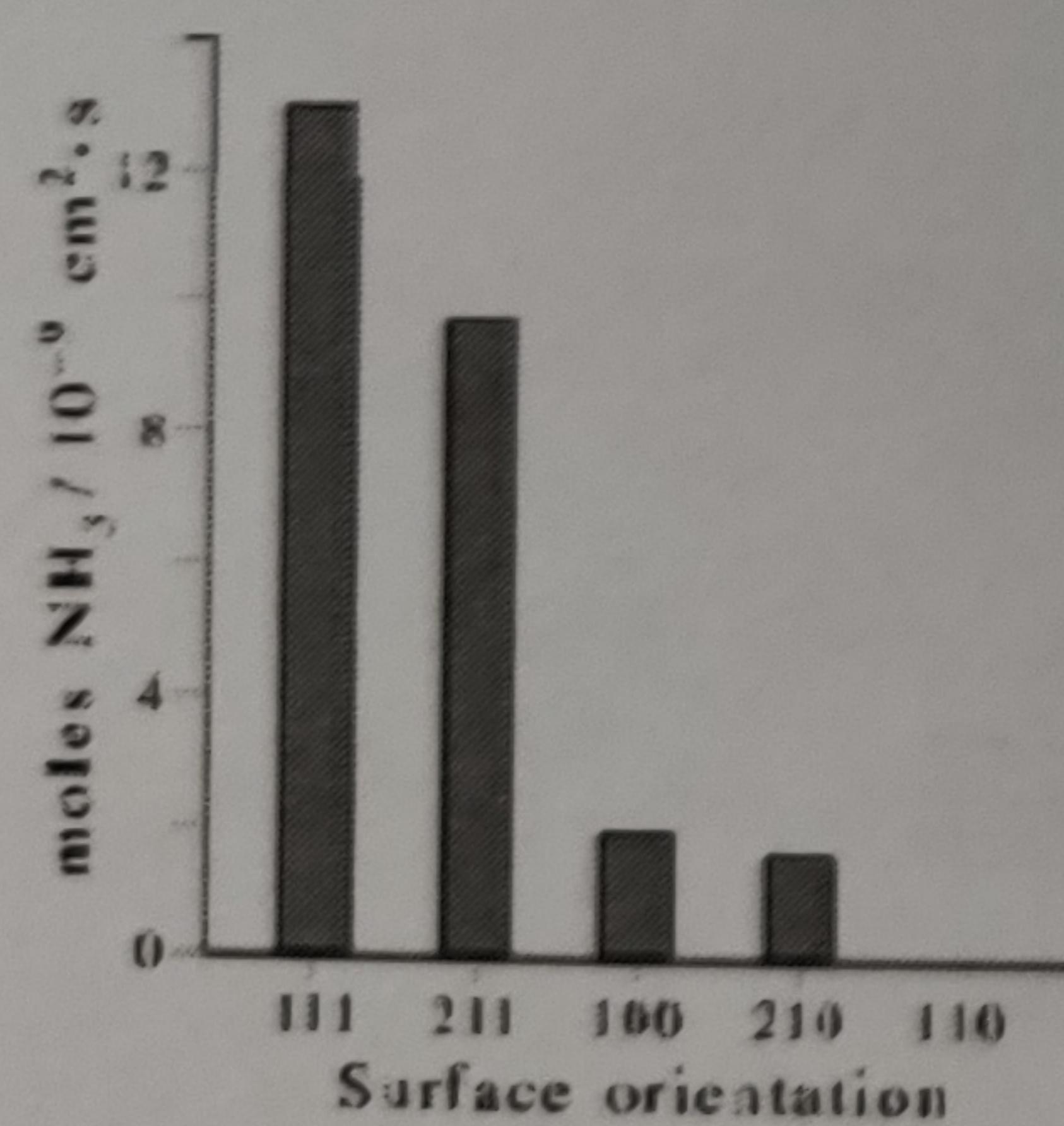
Ammonia Synthesis on Fe Surface



$E_{\text{Dissociation of N}_2}$: 941.6 kJ·mol⁻¹ → ~ 10 kJ·mol⁻¹ (Fe surface)

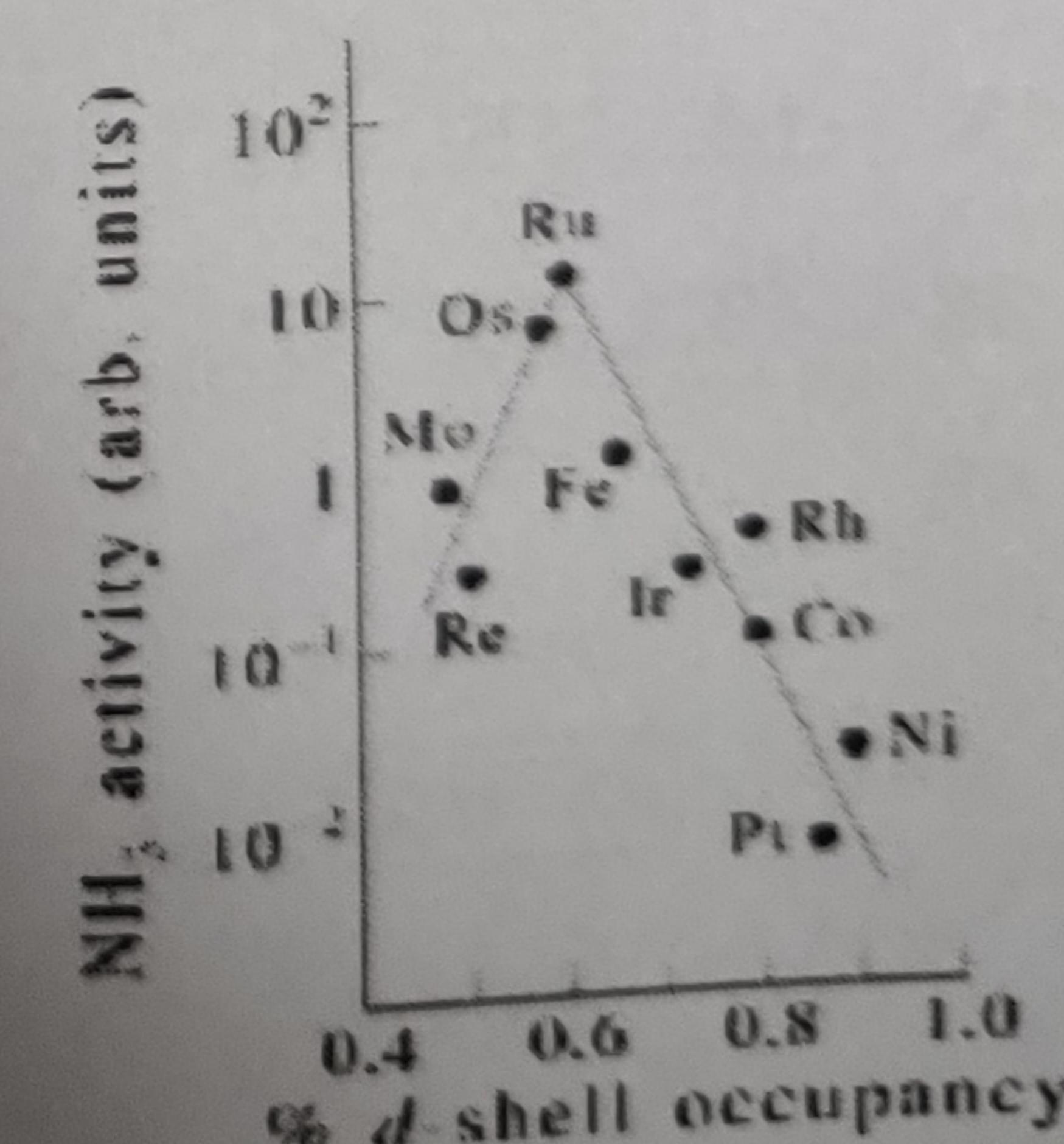


Ammonia Synthesis on Different Fe Surfaces



The highest yield of NH₃ is observed on Fe(111) surface

Volcano Curve



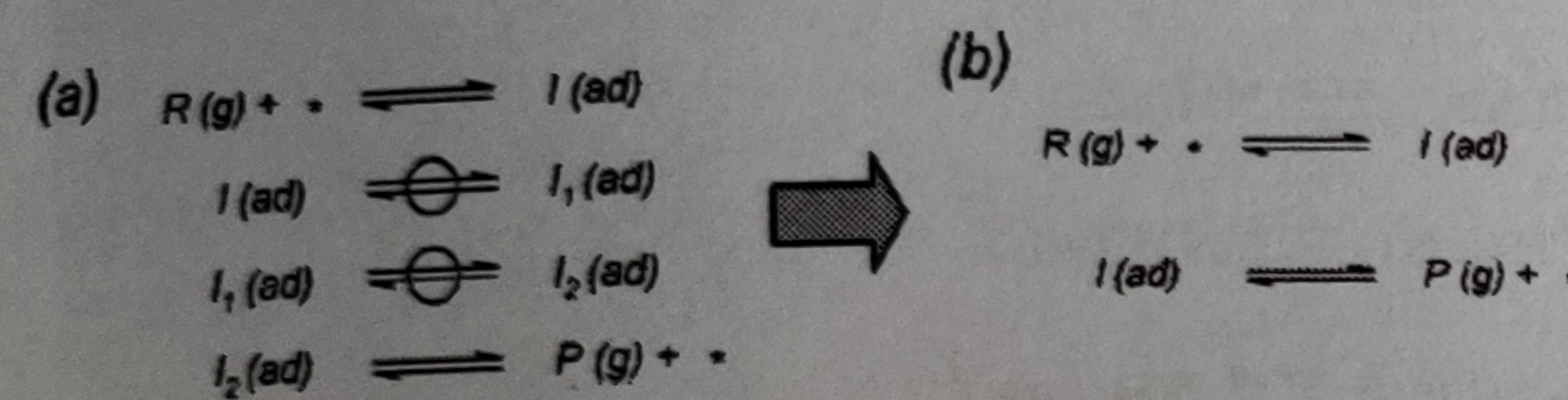
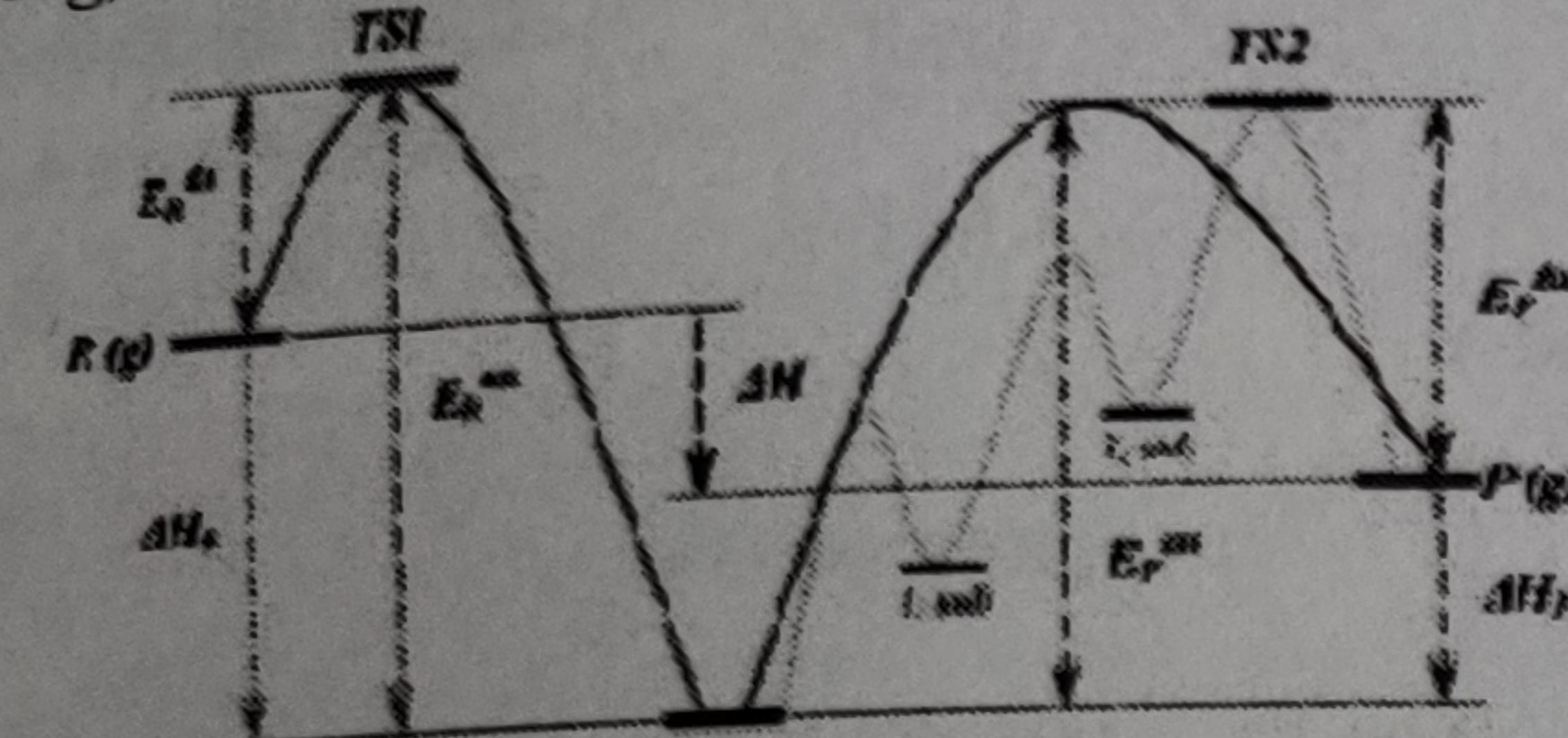
Ammonia synthesis catalyzed by different metals



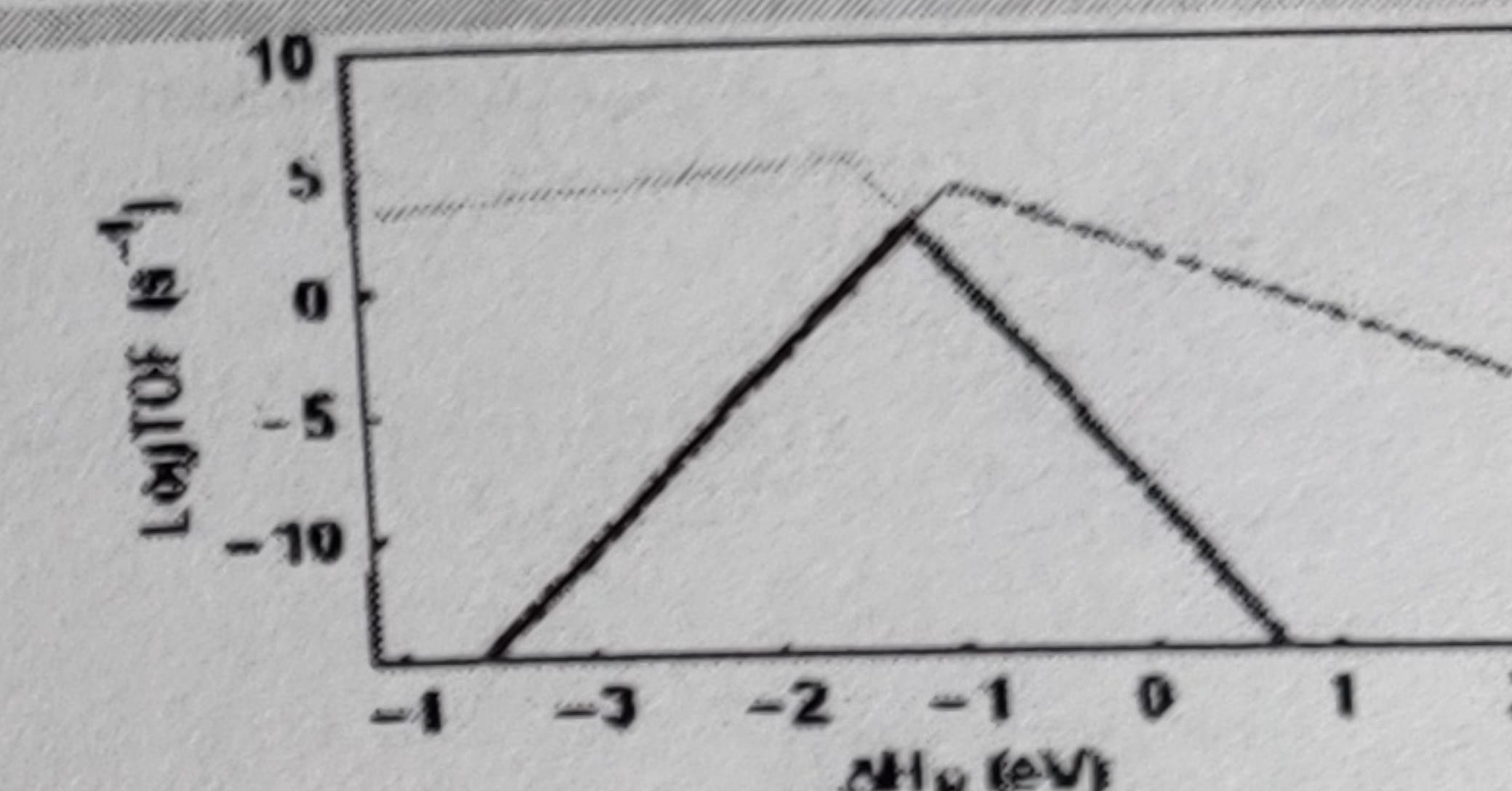
Volcano Curve: Kinetics Analysis

T. Bligaard, et. al., J. Catal. 224, 206 (2004).

J. Cheng, P. Hu, et. al., J. Phys. Chem. C 112, 1308 (2008).



Kinetic model: Multistep surface reactions and desorption (a)
are treated as one-step desorption processes (b)



Reaction rate in terms of turnover frequency (TOF) against ΔH_R

$$v = \frac{k_B T}{h} \frac{1 - \frac{P_P}{P_R} e^{\frac{\Delta G}{RT}}}{\frac{1}{P_R} e^{\frac{S_R}{R}} e^{\frac{E_R^{\text{dis}}}{RT}} \left(1 + e^{-\frac{E_R^{\text{GSS}}}{RT}} \right) + e^{\frac{E_P^{\text{GSS}}}{RT} \left(1 + \frac{P_P}{P_R} e^{\frac{\Delta G}{RT}} e^{\frac{E_R^{\text{GSS}} - E_P^{\text{GSS}}}{RT}} \right)}}$$

- An inert catalyst (less d electrons) is difficult to activate the reactants \rightarrow high adsorption barriers
- An active catalyst (more d electrons) \rightarrow high desorption barriers



Homework:

- 1, 2, 3, 5, 9, 13, 14, 15, 16, 18, 21, 24,
 25, 27, 29, 37, 38, 43, 46, 51, 53, 54, 55,
 57, 58, 61, 65, 68