Microenvironmental Changes

Electrochemical

*Orientation

*Diffusion

*Cathode Reactions

*Anode Reactions

Effect of Potential on Equilibria

(Activation Energy Small)

[C] changes from 10^{-n} to $10^{-(n+1)}$

for

$\Delta V = 59$ mv ($1e^-$ process)

Cathode Processes

*Oxygen Consumption

$$\tfrac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$$ O_2/OH^- -0.3V

*Electrolysis

$$2H^+ + 2e^- \rightarrow H_2$$ H^+/H_2 -1.23V (-1.0)

Anode Processes

*Electrolysis

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$

H_2O/O_2 1.23V(1.0)

*Chlorine release

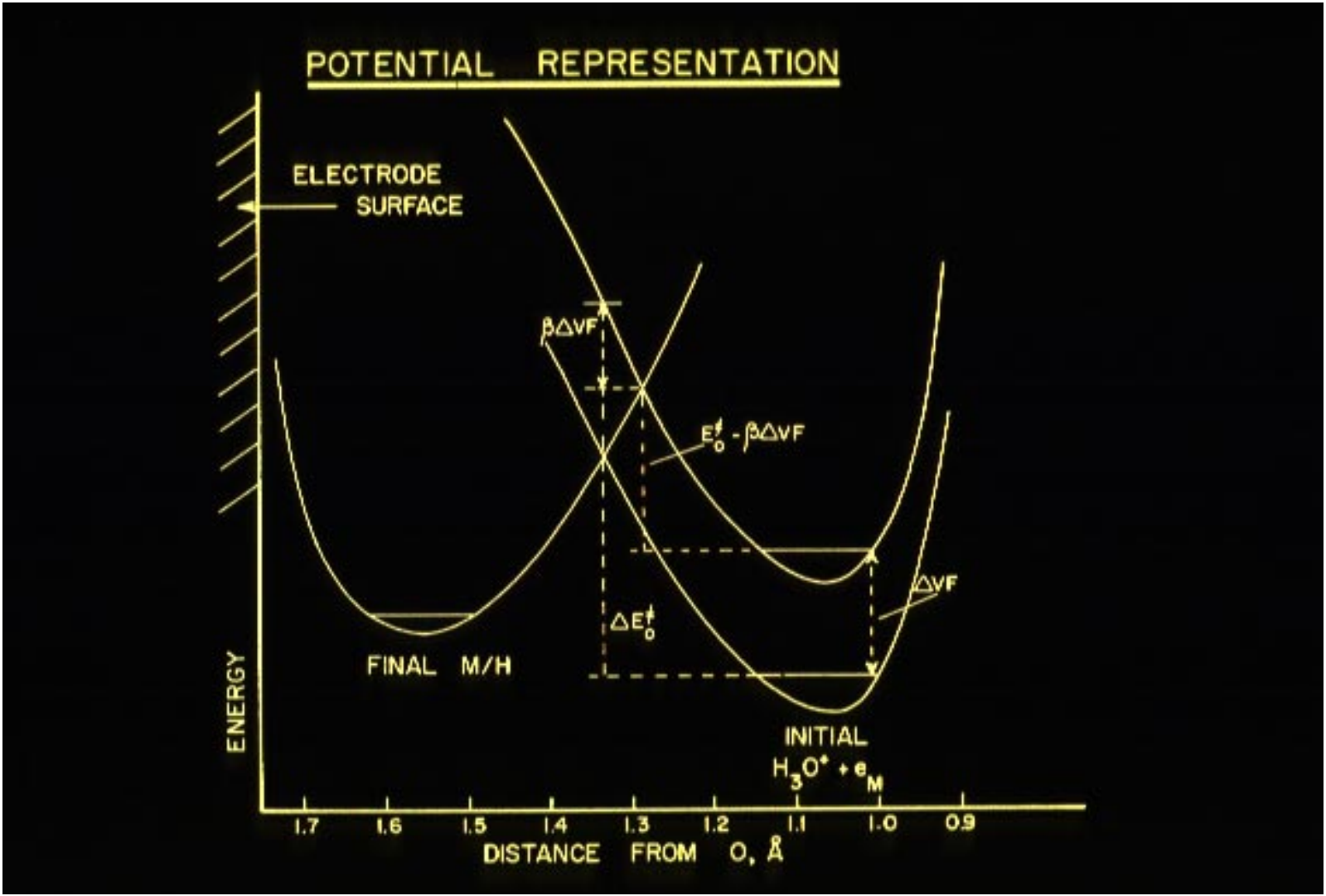
$2Cl^- \rightarrow Cl_2 + 2e^-$ Cl^-/Cl_2 1.36V

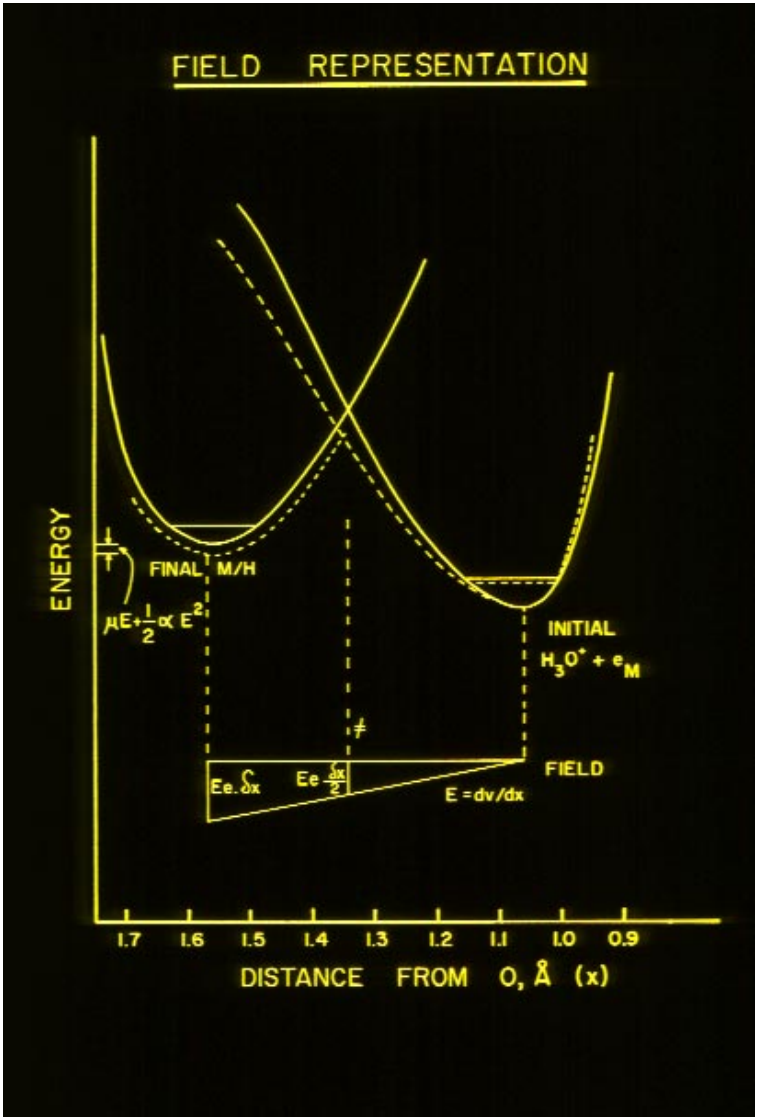
Anode Processes (continued)

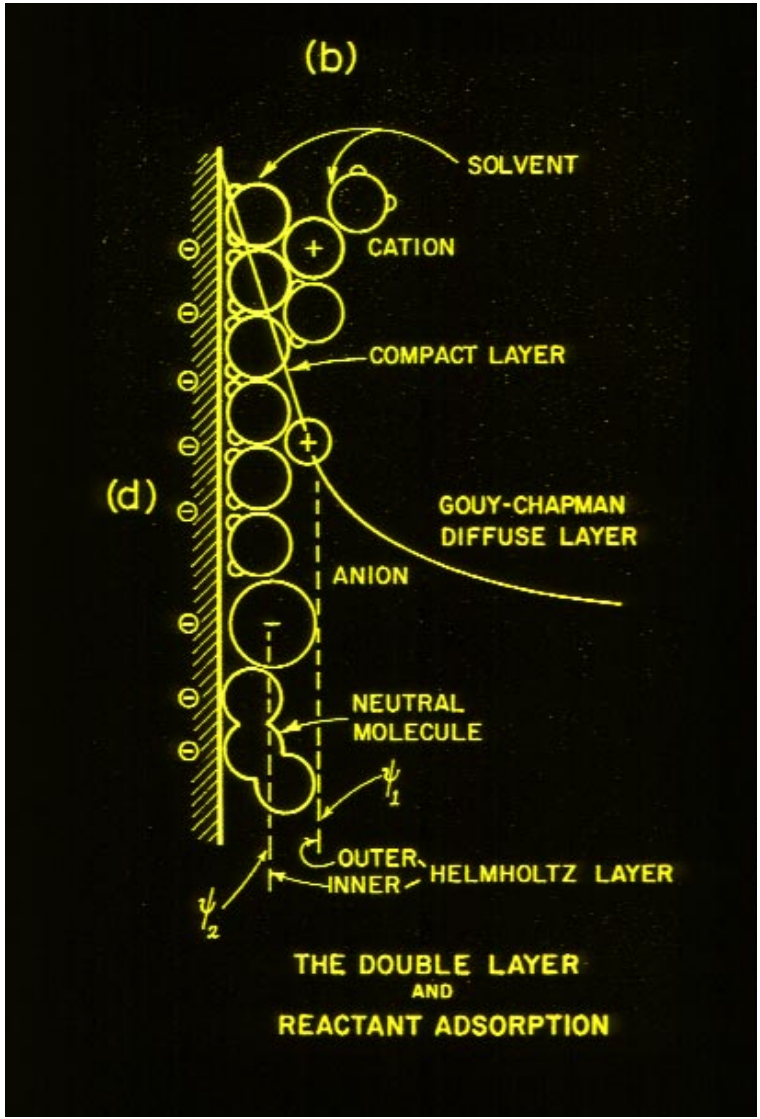
*Metallic Ion Release (Corrosion)

$M^{\circ} \rightarrow M^{+n} + ne^{-}$

Fe/Fe^{+3}	0.04V
Ni/Ni^{+2}	0.23
Co/Co^{+2}	0.28
Cr/Cr^{+3}	0.41
V/V^{+2}	1.2
Mn/Mn^{+2}	1.47
Ti/Ti^{+2}	1.63


POTENTIAL REPRESENTATION
ELECTRODE SURFACE
βΔVF
$E_0^{\ddagger} - \beta\Delta VF$
ΔVF
$\Delta E_0^{\ddagger}$
FINAL M/H
INITIAL
$H_3O^+ + e_M$
ENERGY
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
0.9
DISTANCE FROM O, Å


FIELD REPRESENTATION
ENERGY
FINAL M/H
$\mu E + \frac{1}{2}\alpha E^2$
INITIAL
$H_3O^+ + e_M$
$\neq$
FIELD
$Ee.\delta x$
$Ee.\frac{\delta x}{2}$
$E = dv/dx$
1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9
DISTANCE FROM O, Å (x)


(b)
SOLVENT
CATION
COMPACT LAYER
(d)
GOUY-CHAPMAN
DIFFUSE LAYER
ANION
NEUTRAL
MOLECULE
ψ_1
OUTER
INNER
HELMHOLTZ LAYER
ψ_2
THE DOUBLE LAYER
AND
REACTANT ADSORPTION

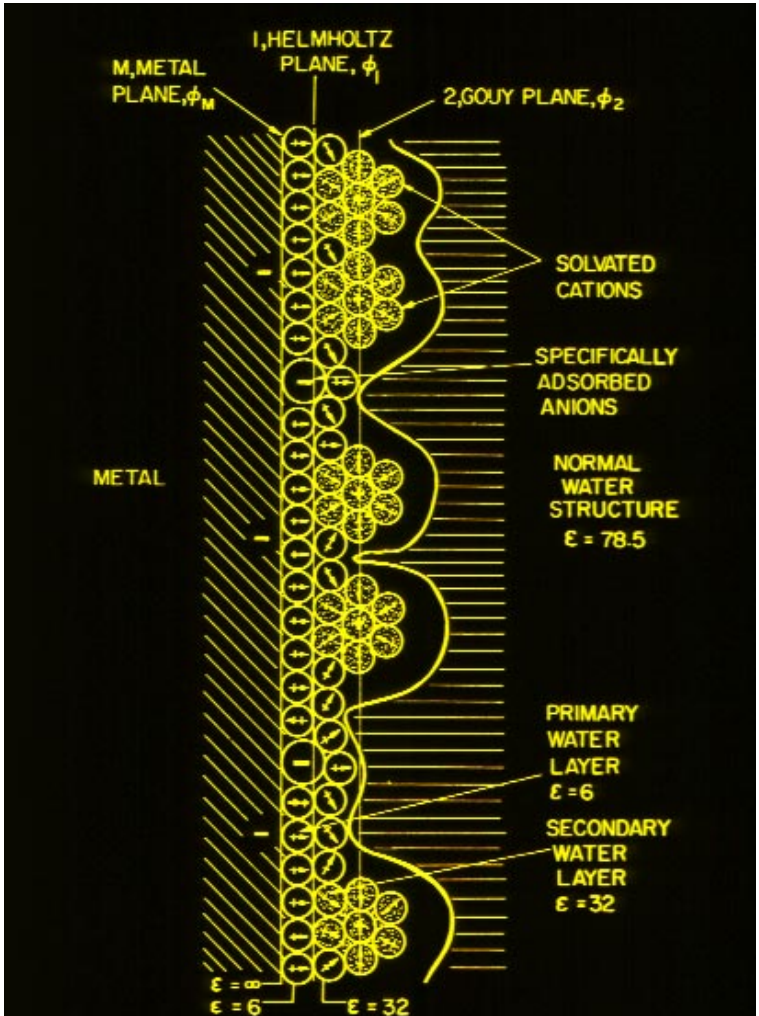
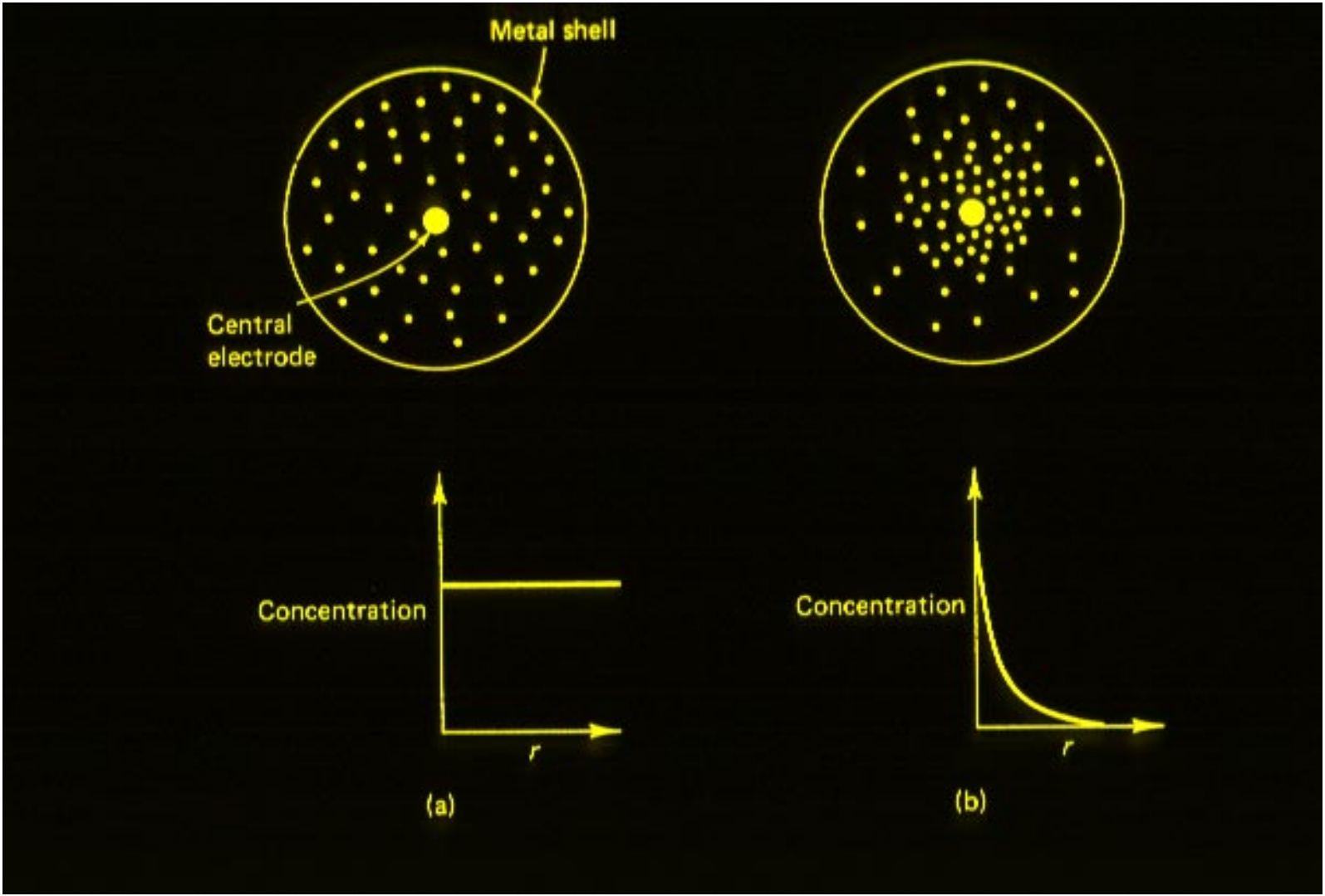
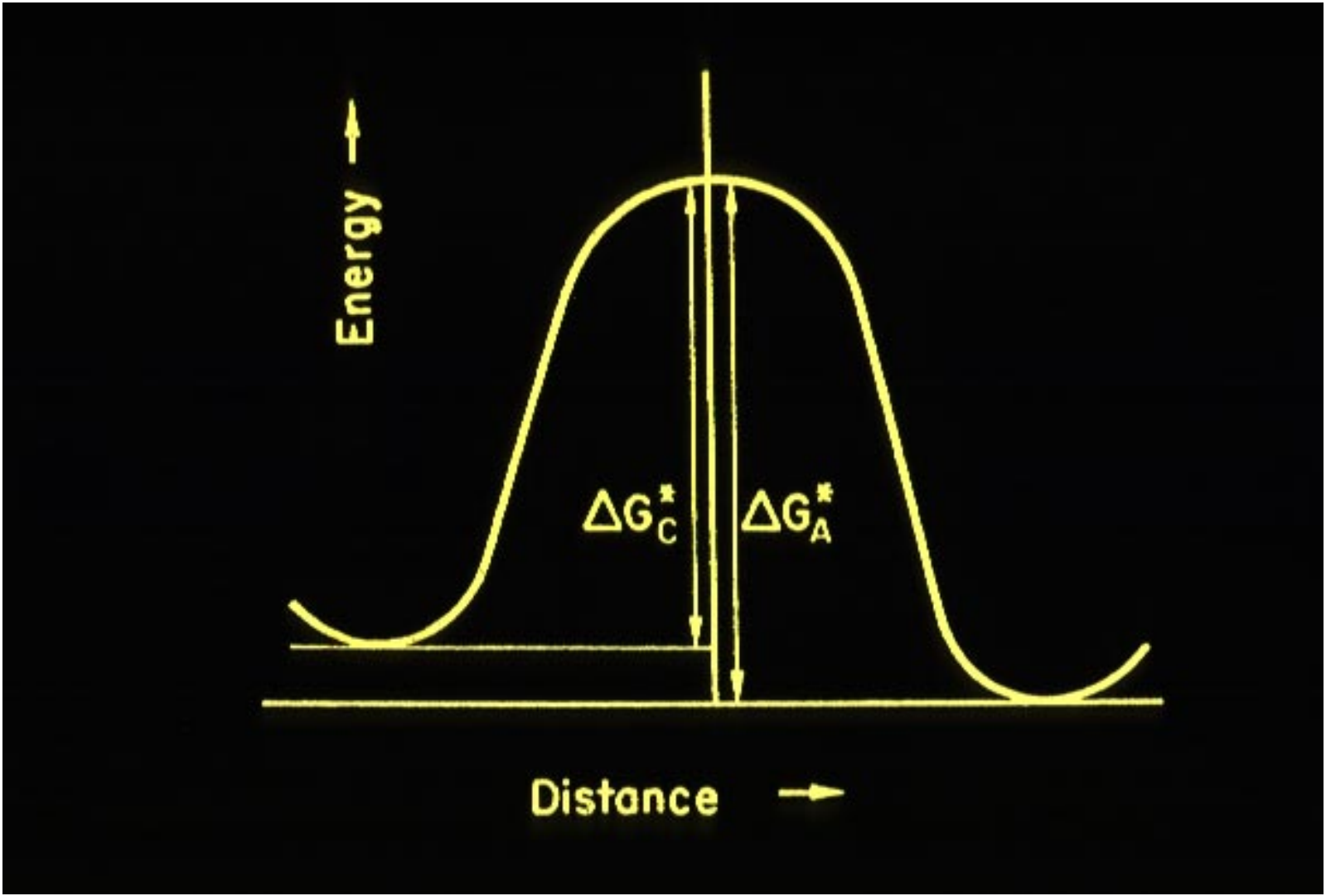
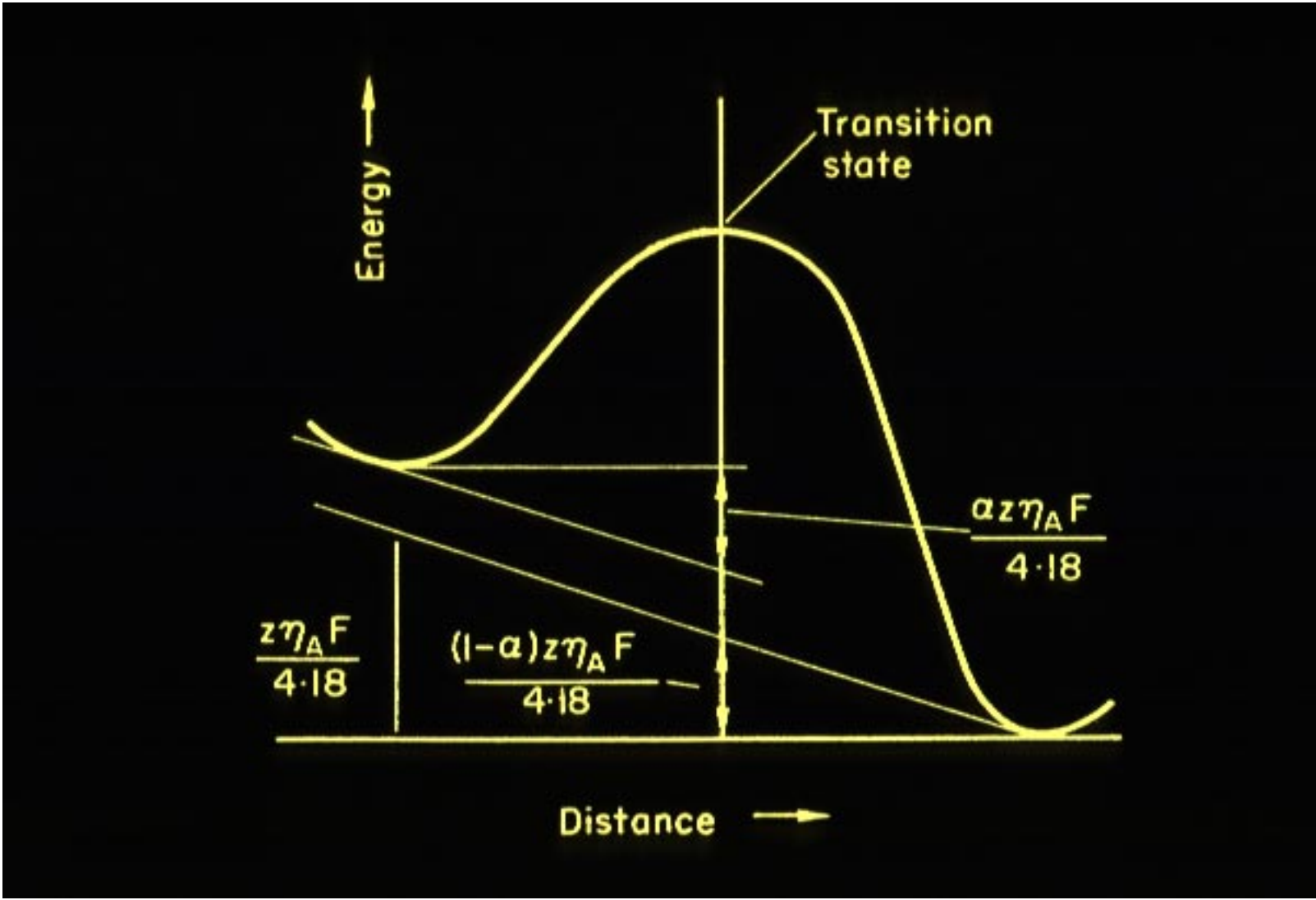


Fig. 7. Solvent adsorption model of the double-layer according to Devanathan, Bockris and Müller (52). (*Proc. Roy. Soc. London* A274, 55.)


Metal shell
Central electrode
Concentration
r
(a)
Concentration
r
(b)


Energy
ΔG_C^*
ΔG_A^*
Distance


Energy
Transition state
$\frac{\alpha z \eta_A F}{4{\cdot}18}$
$\frac{z \eta_A F}{4{\cdot}18}$
$\frac{(1-\alpha) z \eta_A F}{4{\cdot}18}$
Distance

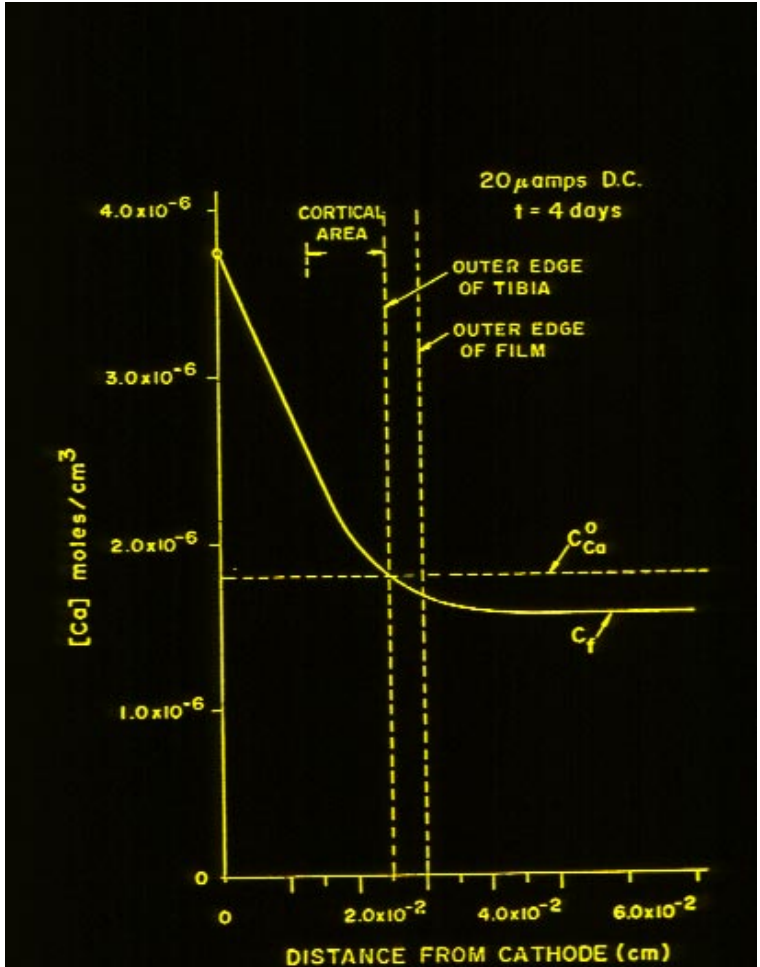

20 μamps D.C.
t = 4 days
CORTICAL AREA
OUTER EDGE OF TIBIA
OUTER EDGE OF FILM
4.0x10⁻⁶
3.0x10⁻⁶
2.0x10⁻⁶
1.0x10⁻⁶
0
[Ca] moles/cm³
C°Ca
Cf
0
2.0x10⁻²
4.0x10⁻²
6.0x10⁻²
DISTANCE FROM CATHODE (cm)

Figure 13-2