ORIGINS OF SELECTIVITY. PART II

KINETIC SELECTIVITY

$$X_X \xrightarrow[cat.]{k_X} P_X$$

ANALYTE

$$\mathbf{X_1 \xrightarrow{k_1} P_1}$$

$$X_2 \xrightarrow{k_2} P_2$$

$$\vdots$$

$$X_n \xrightarrow{k_n} P_n$$

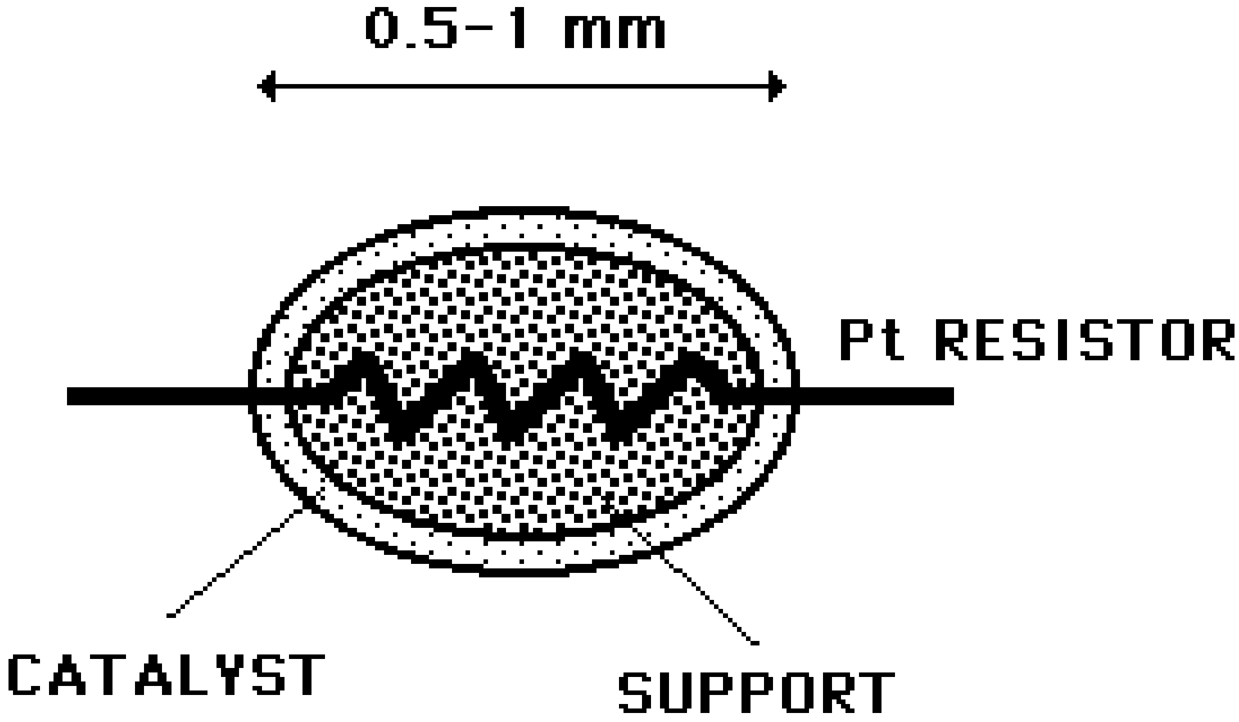
INTERFERANTS

$$k_X >> k_1, k_2 .. k_n$$

• • • USE CATALYSTS

PELLISTOR

$$2CH_4 + 3O_2 \xrightarrow[Pt]{\Delta H} 2CO_2 + H_2O$$



ENZYME SELECTIVITY

- ENZYMES ARE HIGHLY VERSATILE CATALYSTS

$$S + E \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} ES \overset{k_2}{\rightarrow} P$$

- AT STEADY STATE

$$\frac{dC_{ES}}{dt} = k_1 C_S C_E - (k_{-1} + k_2) C_{ES} = 0$$

- MICHAELIS MENTEN

$$v = \frac{v_{\max} C_S}{C_S + K_m}$$

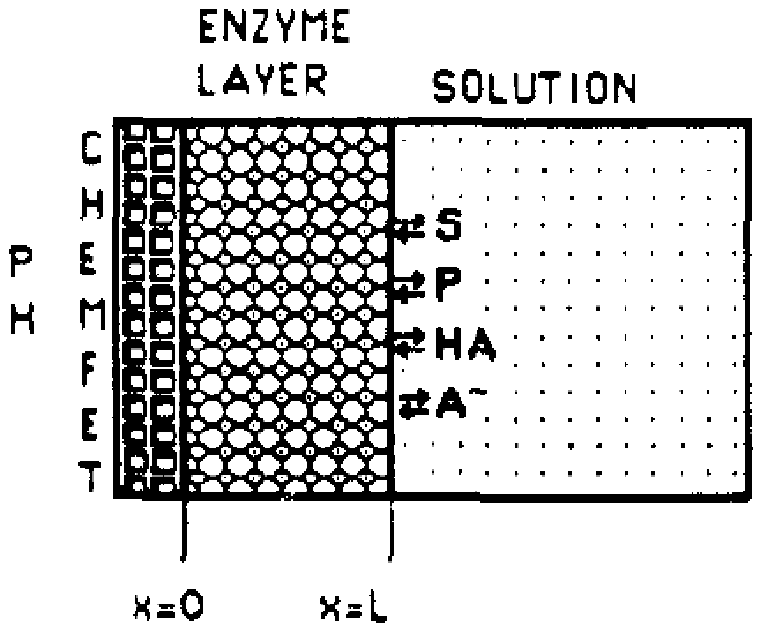
Michaelis-Menten constant K_m is figure of merit of the enzyme

M-M KINETICS

- ENZYMATIC REACTIONS ARE pH DEPENDENT

$$v = \Re_{pH} \frac{v_{\max} C_S}{C_S + K_m} \qquad \Re_{pH} = \left(1 + \frac{C_H}{K_{ES_1}} + \frac{K_{ES_2}}{C_H}\right)$$

- ENZYMATIC SELECTIVITY CAN BE USED WITH ANY TRANSDUCTION PRINCIPLE EXCEPT MASS SENSING



DIFFUSION-REACTION MECHANISM

DIFFUSION - REACTION MECHANISM

- FOR UNI-DIRECTIONAL TRANSPORT CHANGE OF C_S AT X=0 IS

$$\frac{\delta C_S}{\delta t} = D_S \frac{\delta^2 C_S}{\delta x^2} - \frac{\Re_{pH} v_{\max} C_S}{(C_S + K_m)}$$

- AFTER NORMALIZATION

$$\left(\frac{\delta C_S}{\delta t}\right)^* = D_S \left(\frac{\delta C_S}{\delta x^2}\right)^* - \phi^2 \left(\frac{C_S}{1 + C_S}\right)^*$$

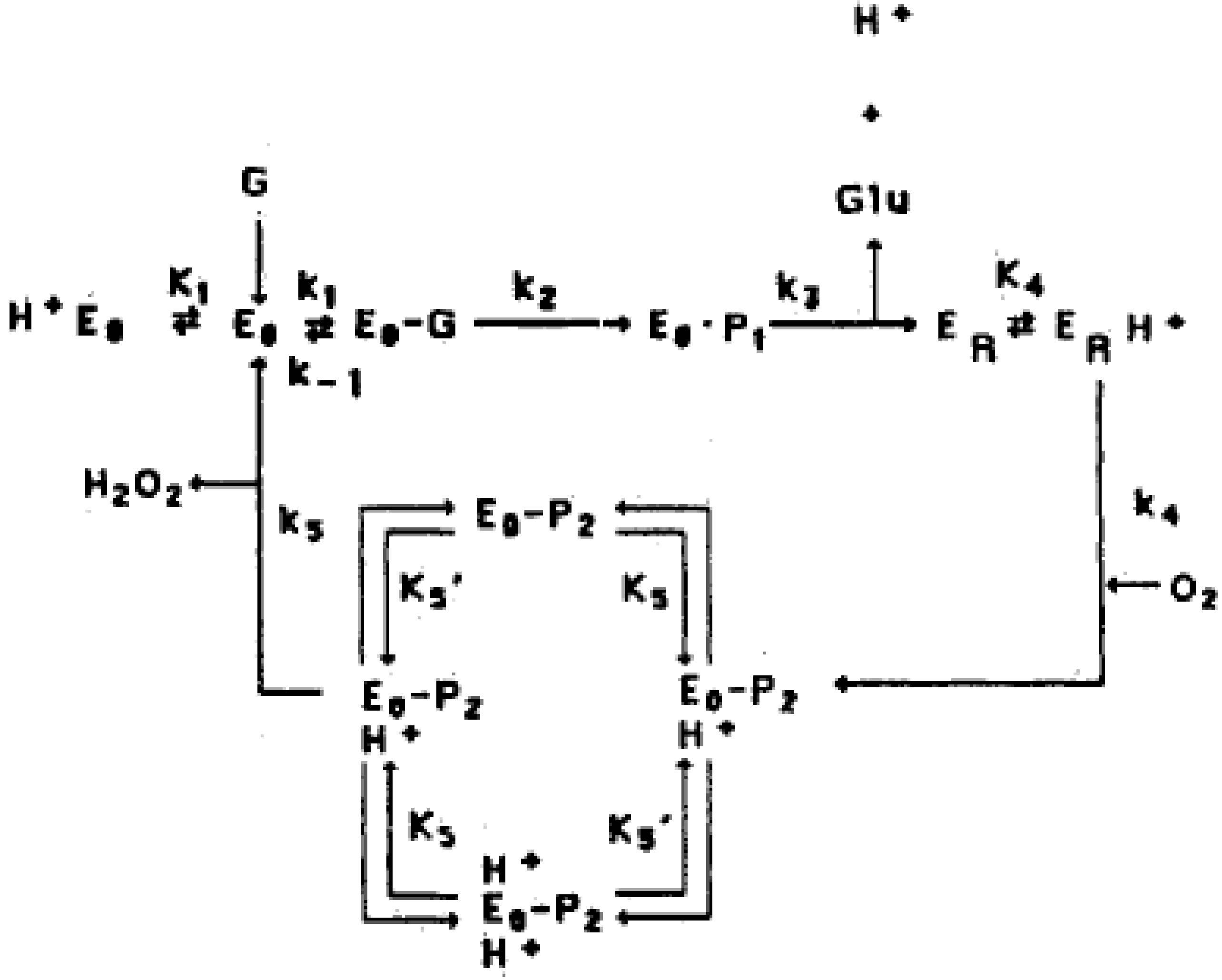
THIELE MODULUS: $$\phi = \frac{L v_{\max}^{1/2}}{(K_m D_S \Re_{pH})^{1/2}}$$

(diffusion control) $10 < \phi < 5$ (reaction control)

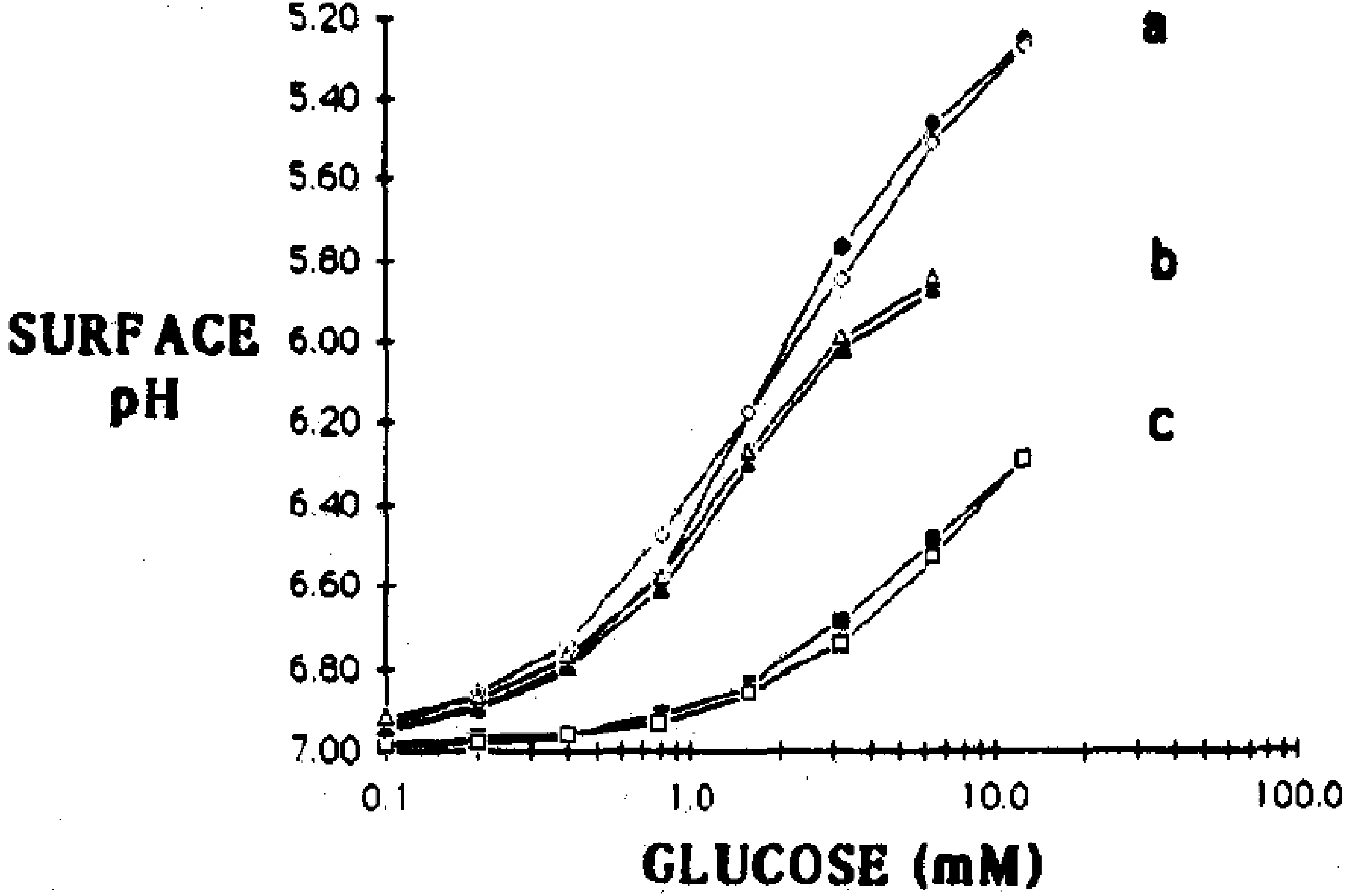
EXAMPLE

GLUCOSE SENSOR

$$C_6H_{12}O_6 \xrightarrow{G.O.D.} C_6H_{12}O_7^- + H^+$$

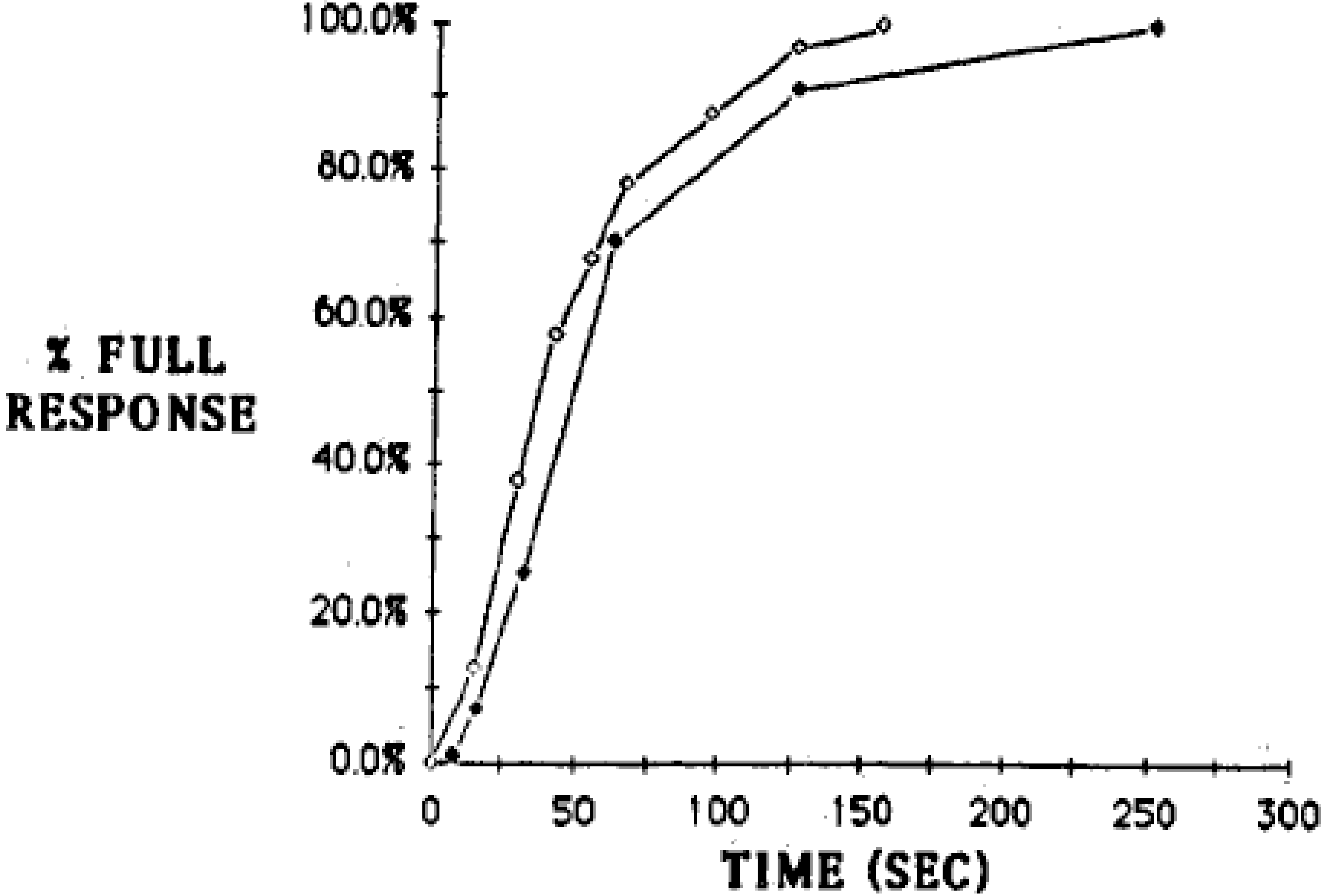


RESPONSE CURVES

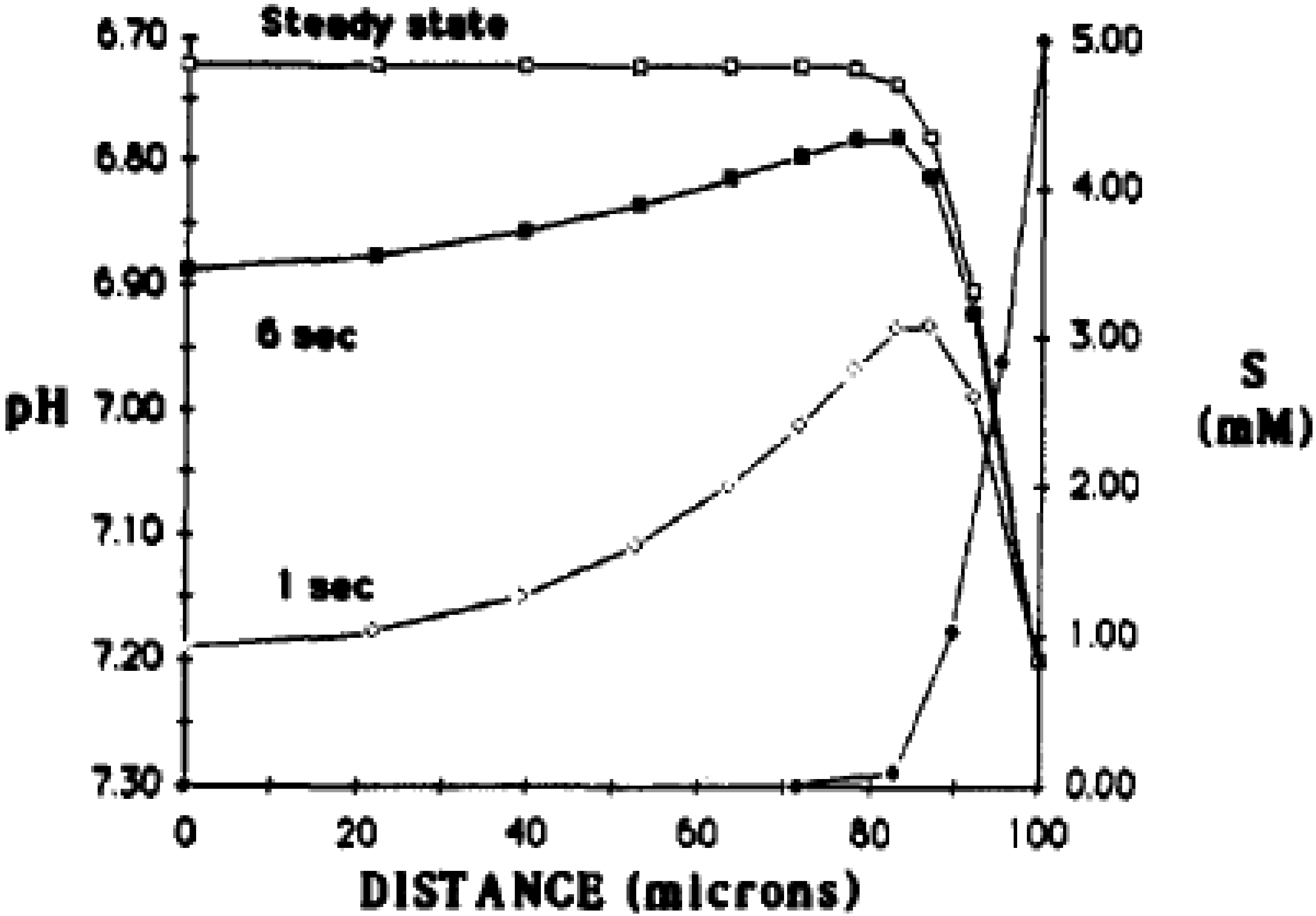


TIME RESPONSE CURVES

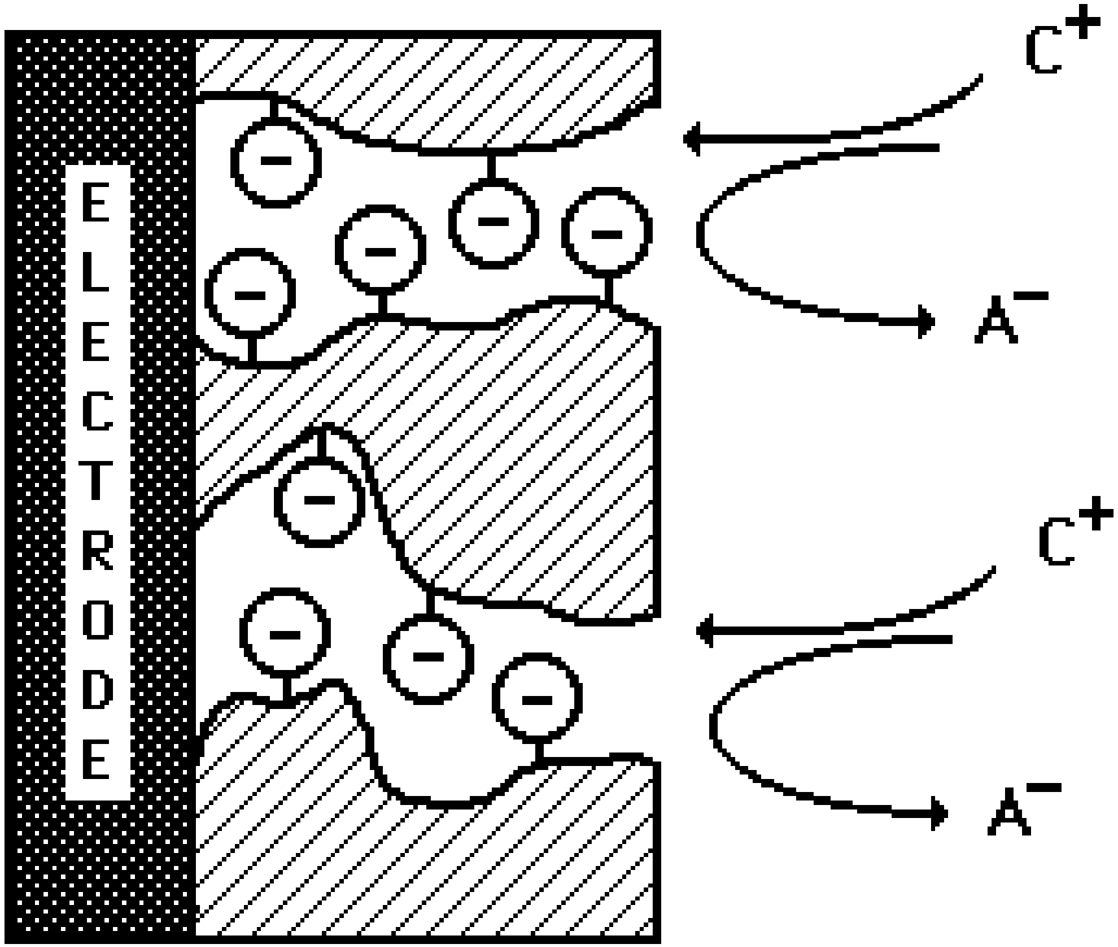
GLUCOSE SENSOR



CONCENTRATION PROFILES



MASS TRANSPORT LIMITED SELECTIVITY
ELECTROSTATIC REJECTION



EXAMPLE

⊖ sulfonate group

A^- ascorbate ion

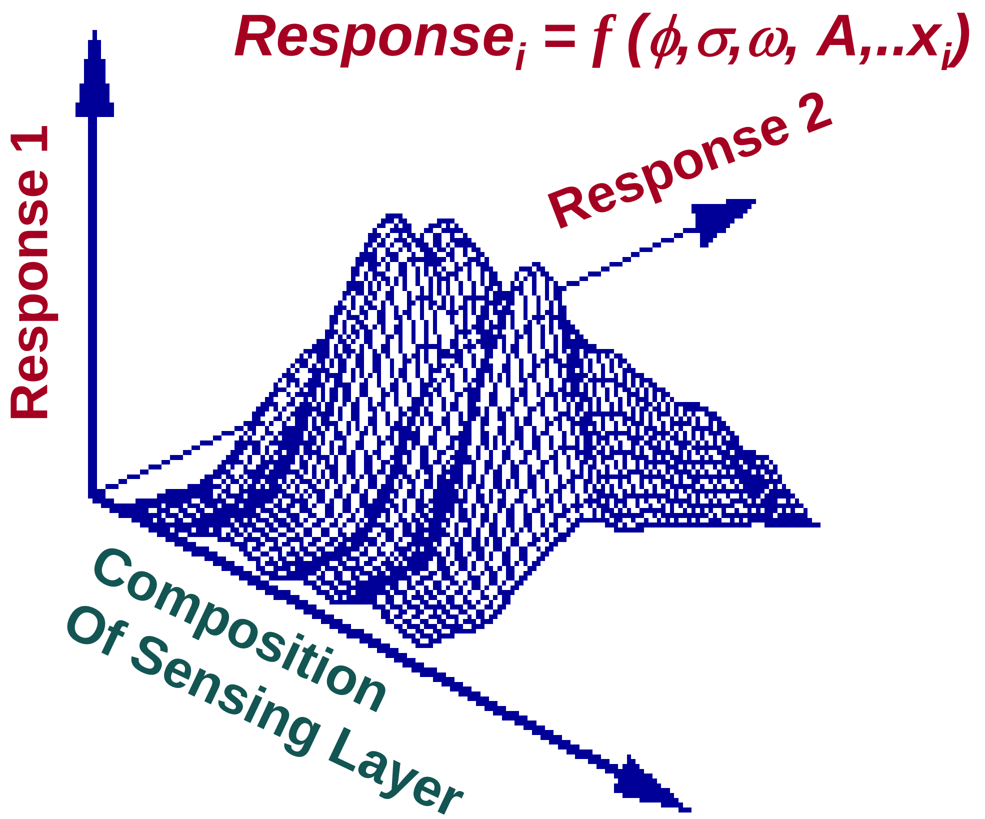
C^+ dopamine

Higher Order Chemical Sensors

Extending the Feature Space in Chemical Sensing

ENVIRONMENTAL
- detection limit
- selectivity
- stability
- dynamic range

PROCESS CONTROL
- speed
- robustness
- safety
- stability



Cost of obtaining the information

must not be higher than the consequences of not having that information