

FIGURE 10: Binding of a ligand molecule to myoglobin. A possible reaction path is indicated by the dashed line. A tentative identification of the barriers and wells with known structural features of Mb is given in subsection 10.2.

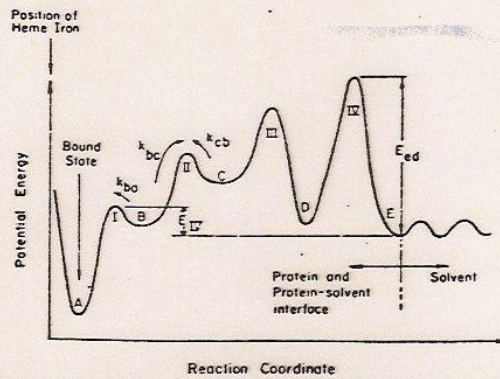


FIGURE 11: Potential encountered by a ligand molecule approaching the heme iron from the solvent. The barriers are numbered I-IV, the wells labeled A-E. The energy E_{ed} , for instance, measures the activation energy for the step $E \rightarrow D$. The energy E_{IV} is defined by eq 48.

The extraction of the rates k_{bc} , k_{cb} , k_{cd} , and k_{dc} at a given temperature from the rebinding curve $N(t)$ is performed by computer. In matrix form and with $k_{ab} = 0$, eq 5 for three barriers ($k_{de} = 0$) is

$$dN/dt = MN \quad (23)$$

where

$$N = \begin{pmatrix} N_a \\ N_b \\ N_c \\ N_d \end{pmatrix}$$

$$M = \begin{pmatrix} 0 & k_{ba} & 0 & 0 \\ 0 & -k_{ba} - k_{bc} & k_{cb} & 0 \\ 0 & k_{bc} & -k_{cb} - k_{cd} & k_{dc} \\ 0 & 0 & k_{cd} & -k_{dc} \end{pmatrix} \quad (24)$$

reflecting

The general solution of eq 23 is found by determining the eigenvalues λ_i and eigenvectors v_i of the eigenvalue equation

$$(M - \lambda_i I)v_i = 0 \quad (25)$$

and expanding

$$N(t) = \sum_{i=1}^4 c_i v_i e^{\lambda_i t} \quad (26)$$

from

Austin, Beeson, Eisenstein,

Fraenfelder + Gunzalus

Biochem. 14, 5355 (1975)

Example 1:
Ligand binding
to myoglobin

DYNAMICS OF LIGAND BINDING TO MYOGLOBIN

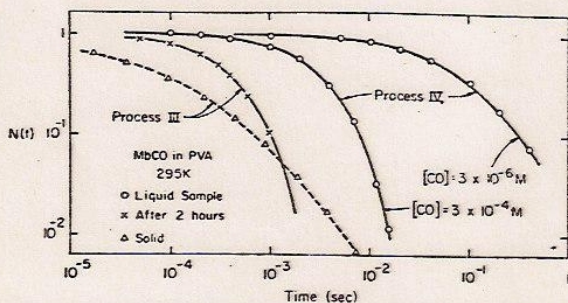


FIGURE 6: Rebinding of CO to Mb in PVA. The curves denoted by IV are obtained in a freshly prepared sample that is still liquid. After about 2-hr drying time, IV disappears and the exponential, but CO independent and faster, process III appears. On complete drying, when PVA becomes solid, the nonexponential curve III is observed.

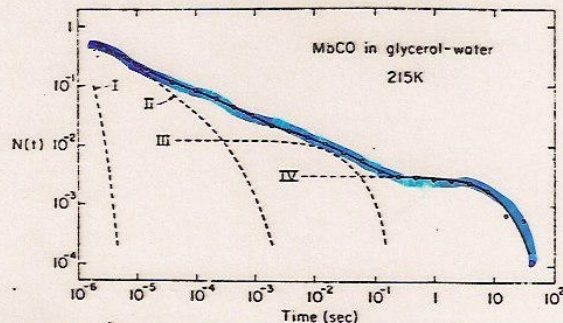
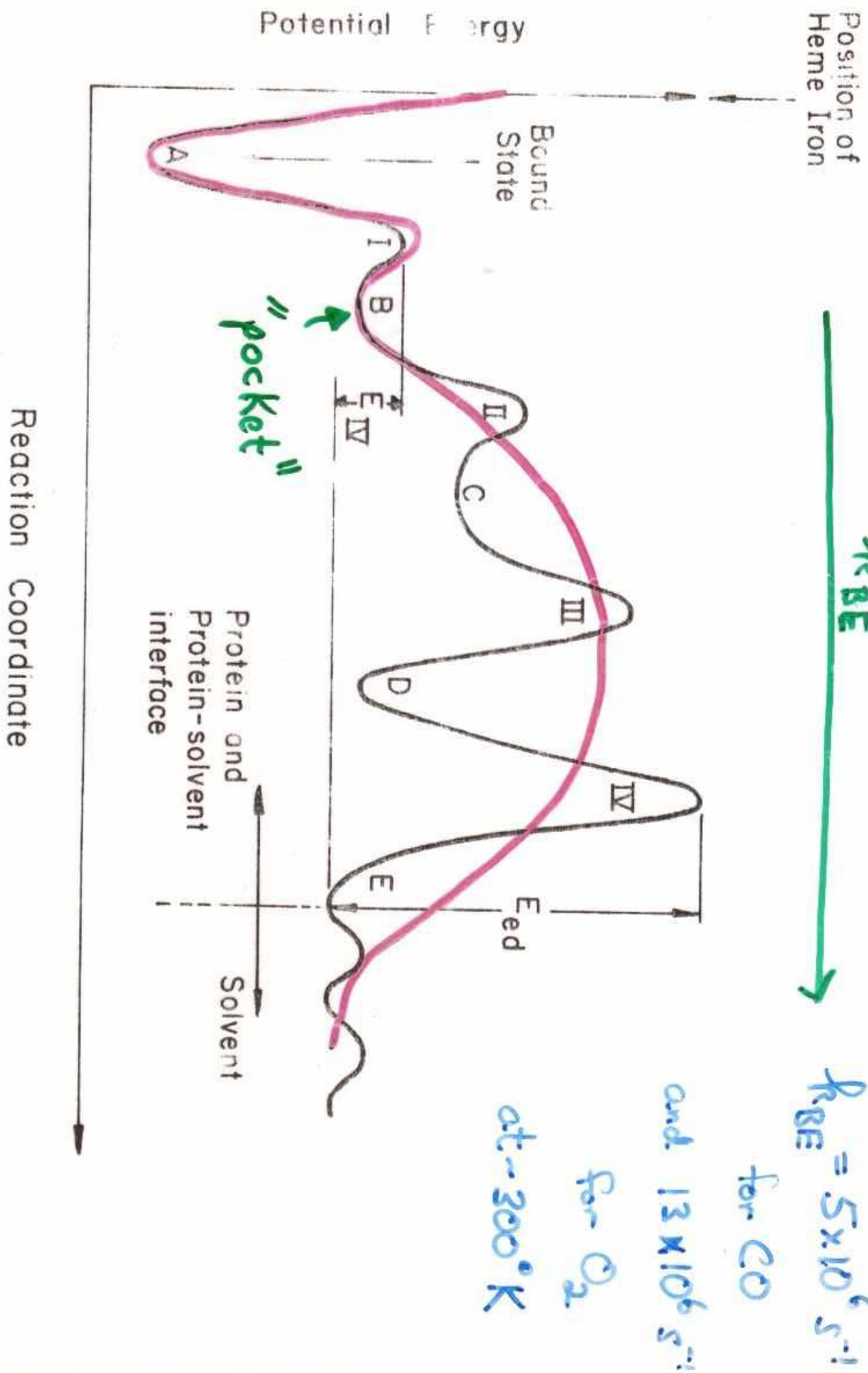


FIGURE 8: Separation of $N(t)$ for $T = 215$ K into the components I-IV. MbCO in glycerol-water, 3:1, v/v. $[CO] = 3 \times 10^{-5} M$. The figure also shows some tentative evidence for a fifth process between II and III.



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