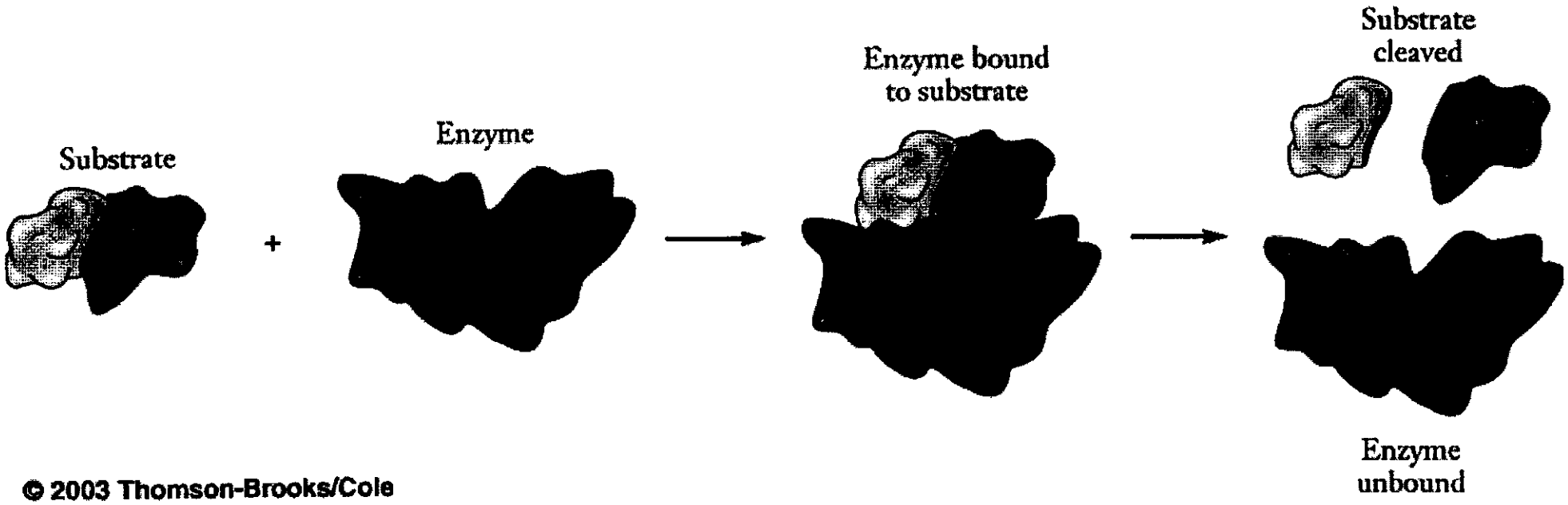
LECTURE 36/36 DEC/06/02

ENZYME CATALYSIS



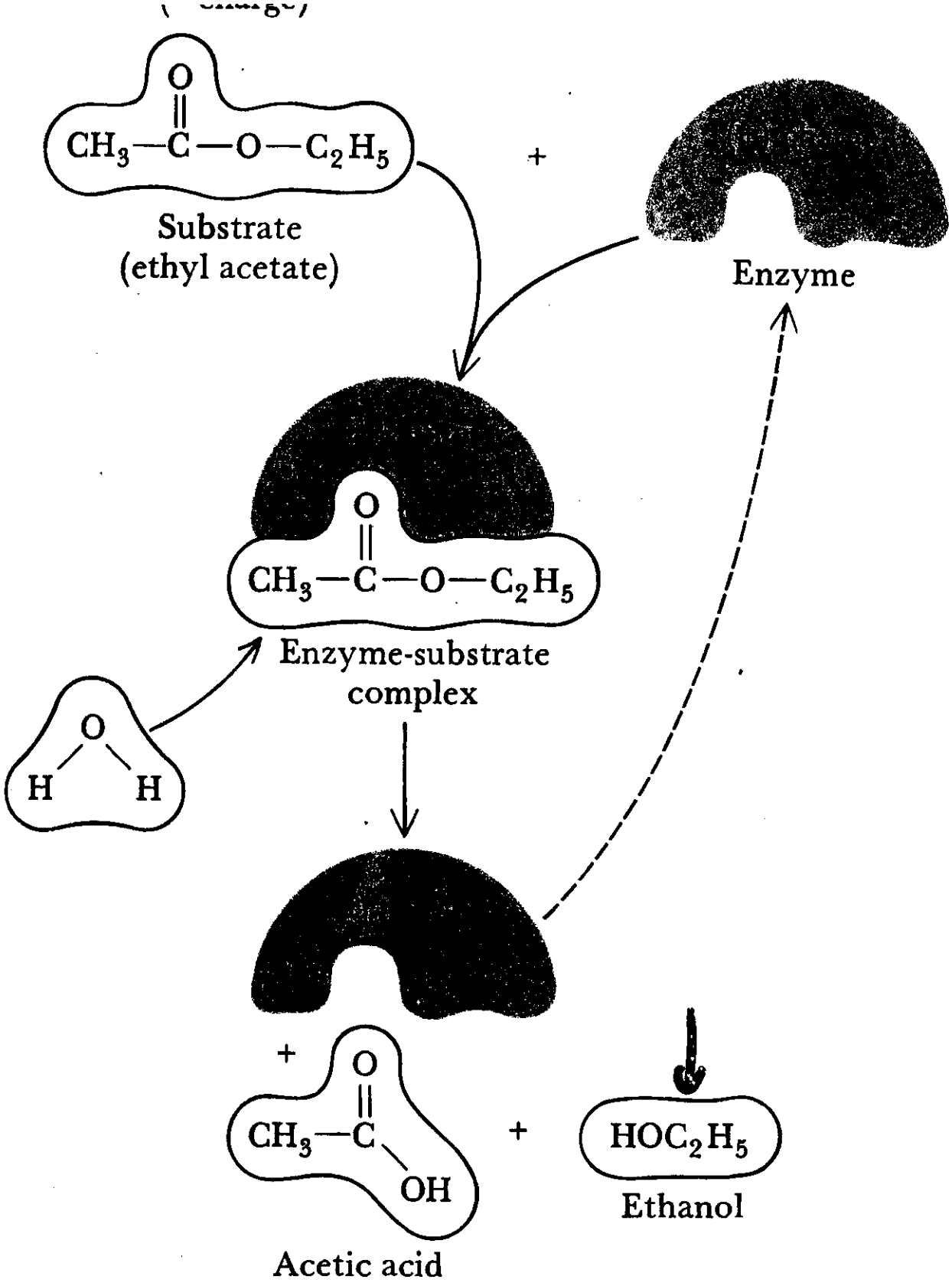
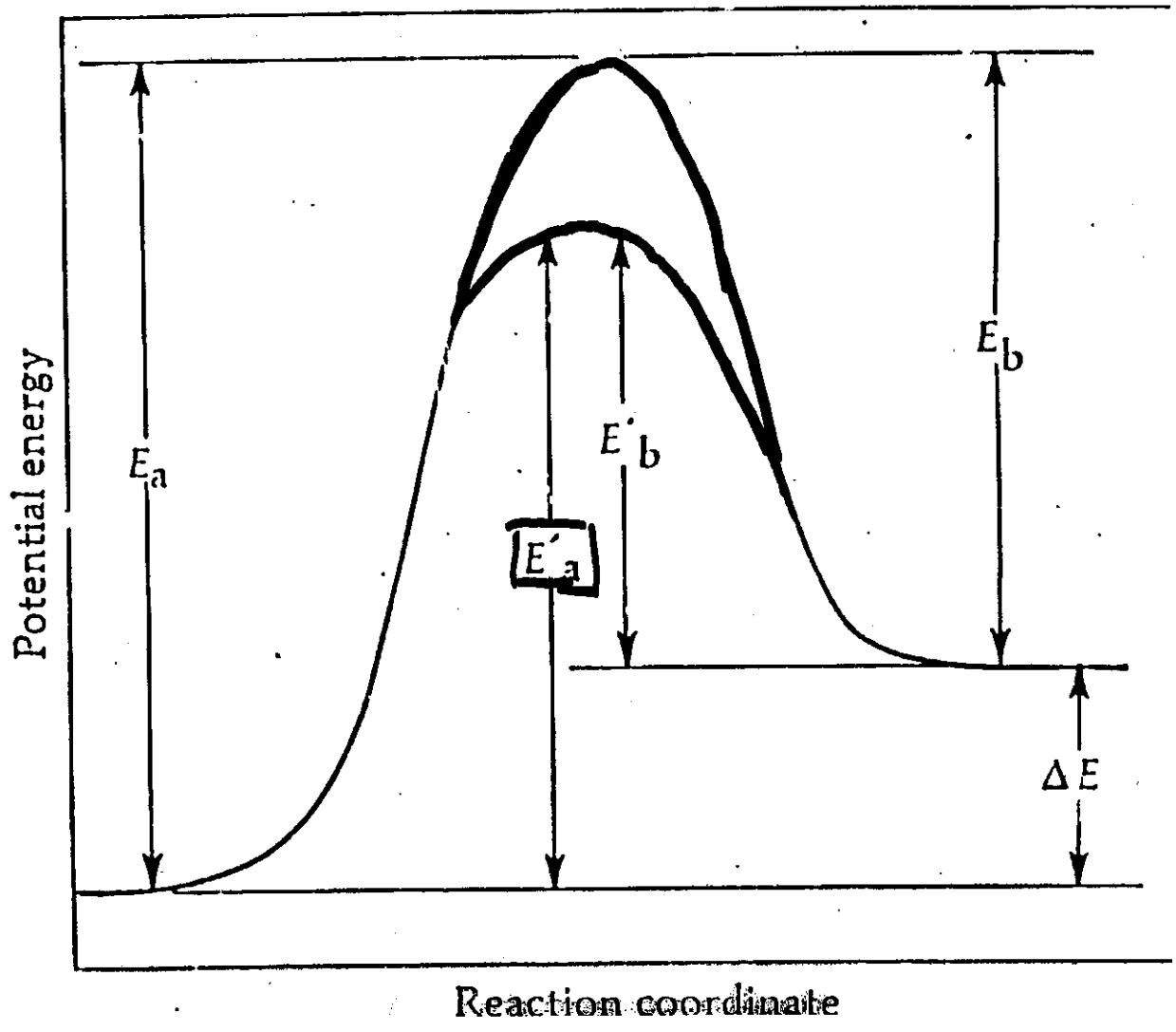


FIGURE 13–9

McQuarrie and Rock: GENERAL CHEMISTRY, Second Edition

FIGURE 2.[illegible] Effect of a catalyst on the potential energy changes occurring in a reaction. The activation energy is lowered from E_a to E'_a. The activation energy of the reverse reaction is lowered to exactly the same extent from E_b to E'_b. The overall energy change ΔE, as well as the equilibrium constant, remain unchanged.



a) $A + B \xrightarrow{E} P_1 + P_2$

$A + B + E_1 \longrightarrow P_1 + P_2 + E_1$

b) $A \xrightarrow{E} P$

$$A + E \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} I$$

$$I \xrightarrow[k_2]{} P$$

$$\frac{dI}{dt} = k_1^+ A \cdot E - k_1^- I - k_2 I \simeq 0$$

$$I = \frac{k_1^+}{k_1^- + k_2} A \cdot E$$

$$\frac{1}{\frac{k_1^- + k_2}{k_1^+}} = \frac{k_1^+}{k_1^- + k_2} = \frac{1}{K_M}$$

$$E_0 = I + E = E\left(1 + \frac{A}{K_M}\right) = \frac{K_A + A}{K_M} E$$

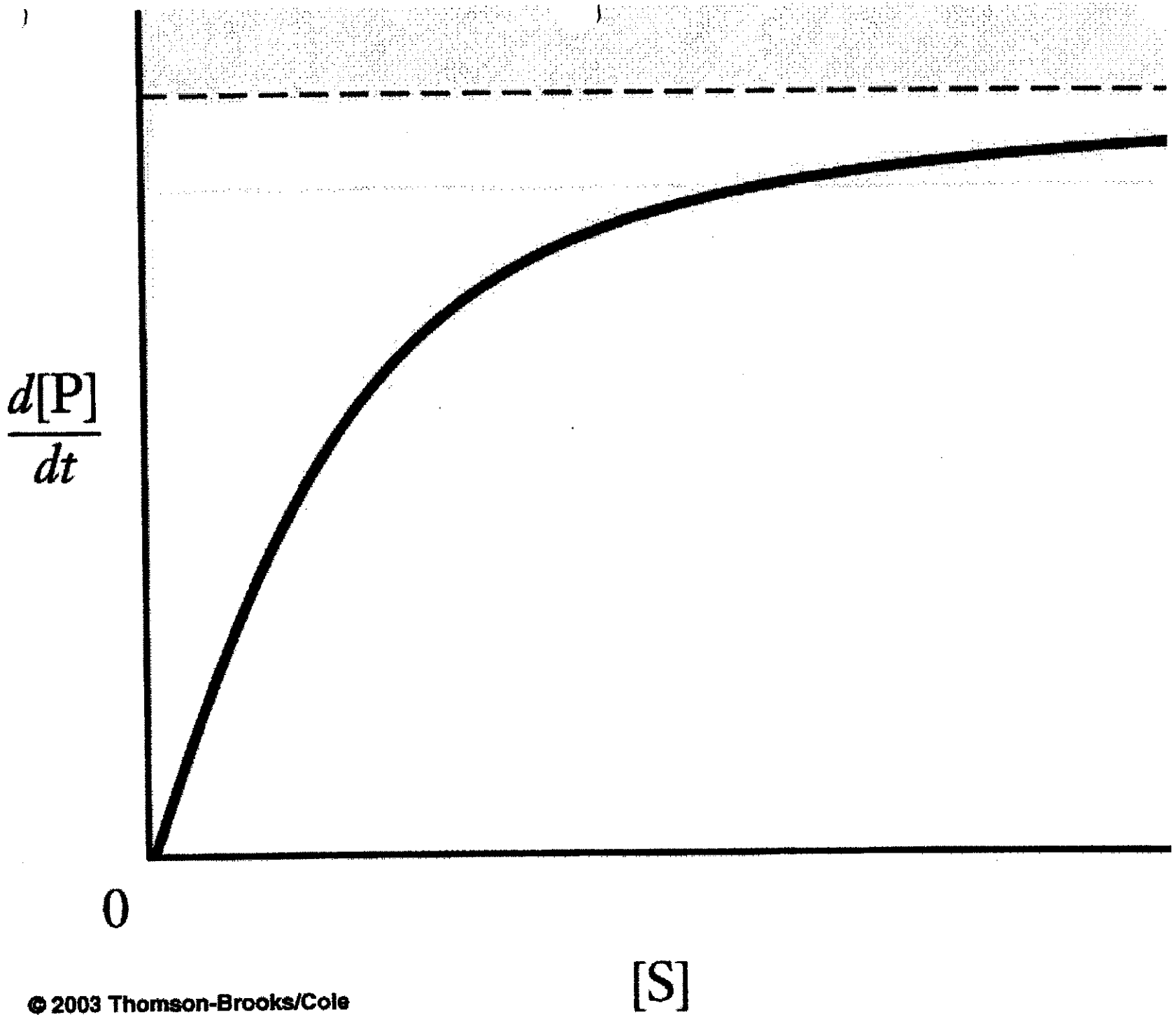
$$\boxed{E = \frac{K_M E_0}{K_A + A}}$$

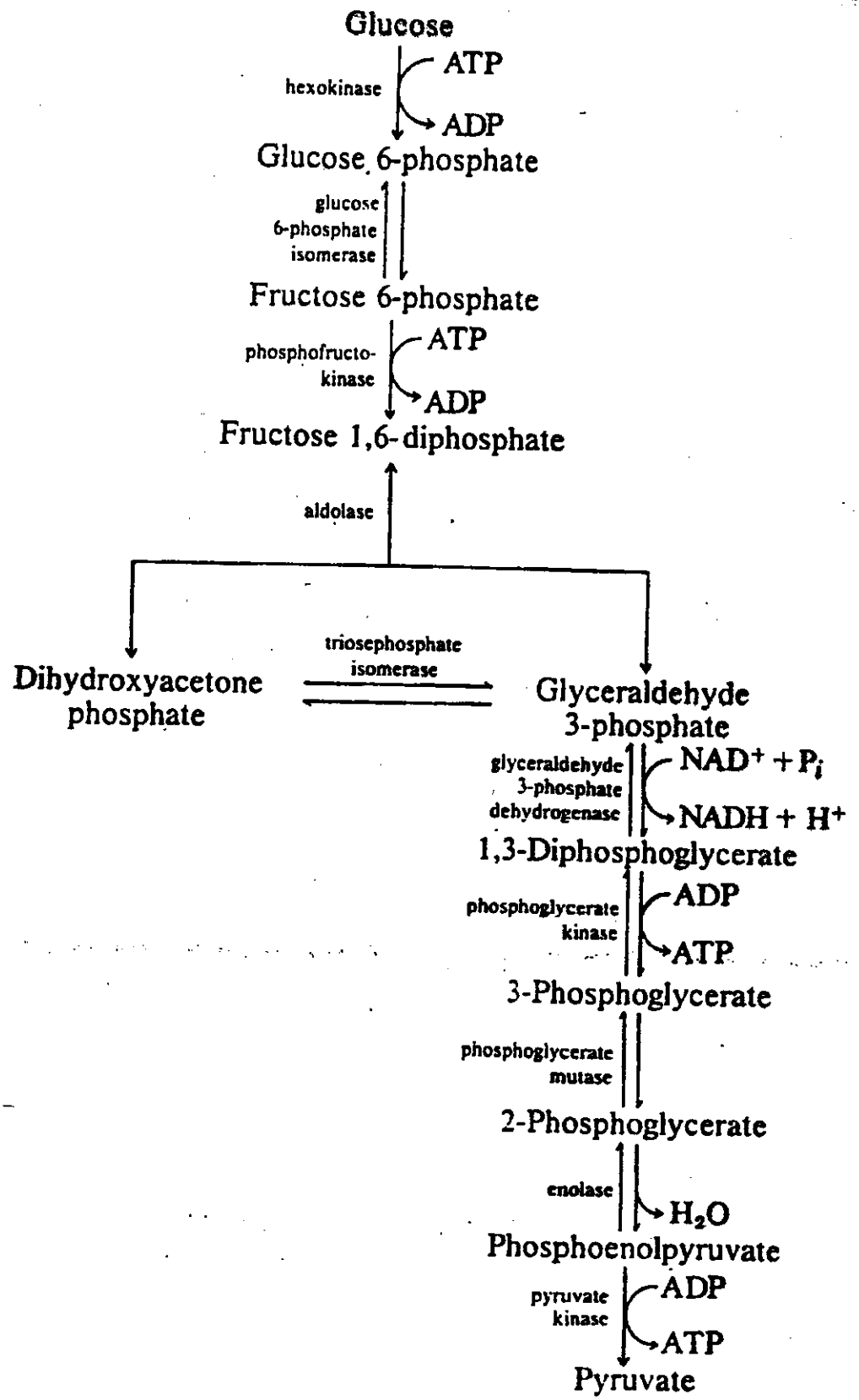
$$r = \frac{dP}{dt} = k_2 I$$

$$= k_2 \frac{A}{K_M} \cdot E = k_2 \frac{A}{K_M} \frac{K_M E_0}{K_M + A}$$

$$r = \frac{k_2 E_0 A}{K_M + A} \equiv \frac{V_0 A}{K_M + A}$$

MICHELIS-MENTEN CONST. K_M





(10-16)

tant control element is the allosteric enzyme phosphofructokinase. It catalyzes the phosphorylation of fructose 6-phosphate to fructose 1,6-diphosphate,

Fructose 6-phosphate + ATP $\rightleftharpoons$

TABLE 12·5. *Metabolite concentrations and K_M's for some glycolytic enzymes*[a]

Enzyme	Source	Substrate	Concentration (μM)	k_M (μM)	$K_M/[S]$
Glucose 6-phosphate isomerase	Brain	G6P	130	210	1.6
	Muscle[b]	G6P	450	700	1.6
		F6P	110	120	1.1
Aldolase	Brain	FDP	200	12	0.06
	Muscle[c]	FDP	32	100	3.1
		G3P	3	1000	333
		DHAP	50	2000	40
Triosephosphate isomerase	Erythrocyte[d]	G3P	18	350	19
	Muscle[e]	G3P	3	460	153
		DHAP	50	870	17
Glyceraldehyde 3-phosphate dehydrogenase	Brain	G3P	3	44	15
	Muscle[f]	G3P	3	70	23
		NAD	600	46	0.08
		P_i	2000		>10
Phosphoglycerate kinase	Brain	1,3DPG	<1	9	>9
		ADP	1500	70	0.05
	Erythrocyte[h]	3PG	118	1100	9.3
	Muscle[i]	3PG	60	1200	200
		ADP	600	350	0.6
Phosphoglycerate mutase	Brain	3PG	40	240	6
	Muscle[j]	3PG	60	5000	83
Enolase	Brain	2PG	4.5	33	7
	Muscle[k]	2PG	7	70	10
Pyruvate kinase[l]	Erythrocyte[m]	PEP	23	200	9
		ADP	138	600	4.4
Lactate dehydrogenase	Brain	Pyr	116	140	1.2
	Erythrocyte[n]	Pyr	51	59	1.2
		Lac	2900	8400	2.9
		NADH	0.01[o]	10[p]	100
		NAD	33	150	4.6
Glycerol phosphate dehydrogenase	Mouse Muscle[q]	Gly-P	170	37	0.22
		Gly-P'	220	190	0.9
		DHAP	50	190	3.8

[a] Abbreviations: G6P = glucose 6-phosphate, F6P = fructose 6-phosphate, FDP = fructose 1,6-diphosphate, G3P = glyceraldehyde 3-phosphate, DHAP = dihydroxyacetone phosphate, P_i = orthophosphate, 1,3DPG = 1,3-diphosphoglycerate, 3PG = 3-phosphoglycerate, 2PG = 2-phosphoglycerate, PEP = phosphoenolpyruvate, Pyr = pyruvate, Lac = lactate (all D-sugars); Gly-P = L-glycerol phosphate. Mouse brain enzymes and mouse brain metabolites from O. H. Lowry and J. V. Passonneau, *J. Biol. Chem.* 239, 31 (1964). Human erythrocyte metabolites from S. Minakami, T. Saito, C. Suzuki, and H. Yoshikawa, *Biochem. Biophys. Res. Commun.* 17, 748 (1964). Human erythrocyte enzymes: see below