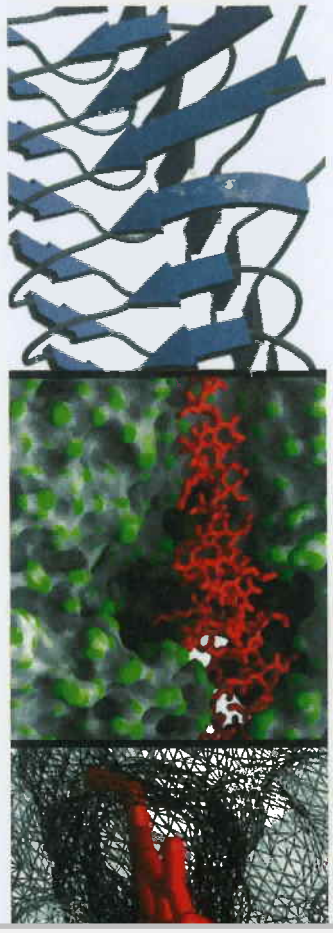
THIRD EDITION

Lehninger Principles of Biochemistry



David L. Nelson
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Cover (from top to bottom): Cut-away view of GroEL, a protein complex involved in protein folding; cut-away view of tobacco mosaic virus, an RNA virus; ribbon model of a β-barrel structural domain from UDP *N*-acetylglucosamine acyltransferase; cut-away view of the F_1 subunit of ATP synthase, with bound ATP shown as a stick structure; mesh surface image of the electron-transfer protein cytochrome *c*, with its heme group shown as a stick structure.

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15. Rates of Turnover of γ and β Phosphates of ATP If a small amount of ATP labeled with radioactive phosphorus in the terminal position, [γ-^{32}P]ATP, is added to a yeast extract, about half of the ^{32}P activity is found in P_i within a few minutes, but the concentration of ATP remains unchanged. Explain. If the same experiment is carried out using ATP labeled with ^{32}P in the central position, [β-^{32}P]ATP, the ^{32}P does not appear in P_i within such a short time. Why?

16. Cleavage of ATP to AMP and PP_i during Metabolism The synthesis of the activated form of acetate (acetyl-CoA) is carried out in an ATP-dependent process:

$$\text{Acetate} + \text{CoA} + \text{ATP} \longrightarrow \text{acetyl-CoA} + \text{AMP} + PP_i$$

(a) The $\Delta G'^\circ$ for the hydrolysis of acetyl-CoA to acetate and CoA is -32.2 kJ/mol and that for hydrolysis of ATP to AMP and PP_i is -30.5 kJ/mol. Calculate $\Delta G'^\circ$ for the ATP-dependent synthesis of acetyl-CoA.

(b) Almost all cells contain the enzyme inorganic pyrophosphatase, which catalyzes the hydrolysis of PP_i to P_i. What effect does the presence of this enzyme have on the synthesis of acetyl-CoA? Explain.

17. Energy for H^+ Pumping The parietal cells of the stomach lining contain membrane "pumps" that transport hydrogen ions from the cytosol of these cells (pH 7.0) into the stomach, contributing to the acidity of gastric juice (pH 1.0). Calculate the free energy required to transport 1 mol of hydrogen ions through these pumps. (Hint: See Chapter 13.) Assume a temperature of 25 °C.

18. Standard Reduction Potentials The standard reduction potential, E'°, of any redox pair is defined for the half-cell reaction:

$$\text{Oxidizing agent} + n\ \text{electrons} \longrightarrow \text{reducing agent}$$

The E'° values for the NAD^+/NADH and pyruvate/lactate conjugate redox pairs are -0.32 and -0.19 V, respectively.

(a) Which conjugate pair has the greater tendency to lose electrons? Explain.

(b) Which is the stronger oxidizing agent? Explain.

(c) Beginning with 1 M concentrations of each reactant and product at pH 7, in which direction will the following reaction proceed?

$$\text{Pyruvate} + \text{NADH} + H^+ \rightleftharpoons \text{lactate} + NAD^+$$

(d) What is the standard free-energy change ($\Delta G'^\circ$) at 25 °C for the conversion of pyruvate to lactate?

(e) What is the equilibrium constant (K'_{eq}) for this reaction?

19. Energy Span of the Respiratory Chain Electron transfer in the mitochondrial respiratory chain may be represented by the net reaction equation

$$\text{NADH} + H^+ + \tfrac{1}{2}O_2 \rightleftharpoons H_2O + NAD^+$$

(a) Calculate the value of $\Delta E'^\circ$ for the net reaction of mitochondrial electron transfer.

(b) Calculate $\Delta G'^\circ$ for this reaction.

(c) How many ATP molecules can *theoretically* be generated by this reaction if the free energy of ATP synthesis under cellular conditions is 52 kJ/mol?

20. Dependence of Electromotive Force on Concentrations Calculate the electromotive force (in volts) registered by an electrode immersed in a solution containing the following mixtures of NAD^+ and NADH at pH 7.0 and 25 °C, with reference to a half-cell of E'° 0.00 V.

(a) 1.0 mM NAD^+ and 10 mM NADH

(b) 1.0 mM NAD^+ and 1.0 mM NADH

(c) 10 mM NAD^+ and 1.0 mM NADH

21. Electron Affinity of Compounds List the following substances in order of increasing tendency to accept electrons: (a) α-ketoglutarate + CO_2 (yielding isocitrate); (b) oxaloacetate; (c) O_2; (d) $NADP^+$.

22. Direction of Oxidation-Reduction Reactions Which of the following reactions would you expect to proceed in the direction shown under standard conditions, assuming that the appropriate enzymes are present to catalyze them?

(a) $\text{Malate} + NAD^+ \longrightarrow \text{oxaloacetate} + \text{NADH} + H^+$

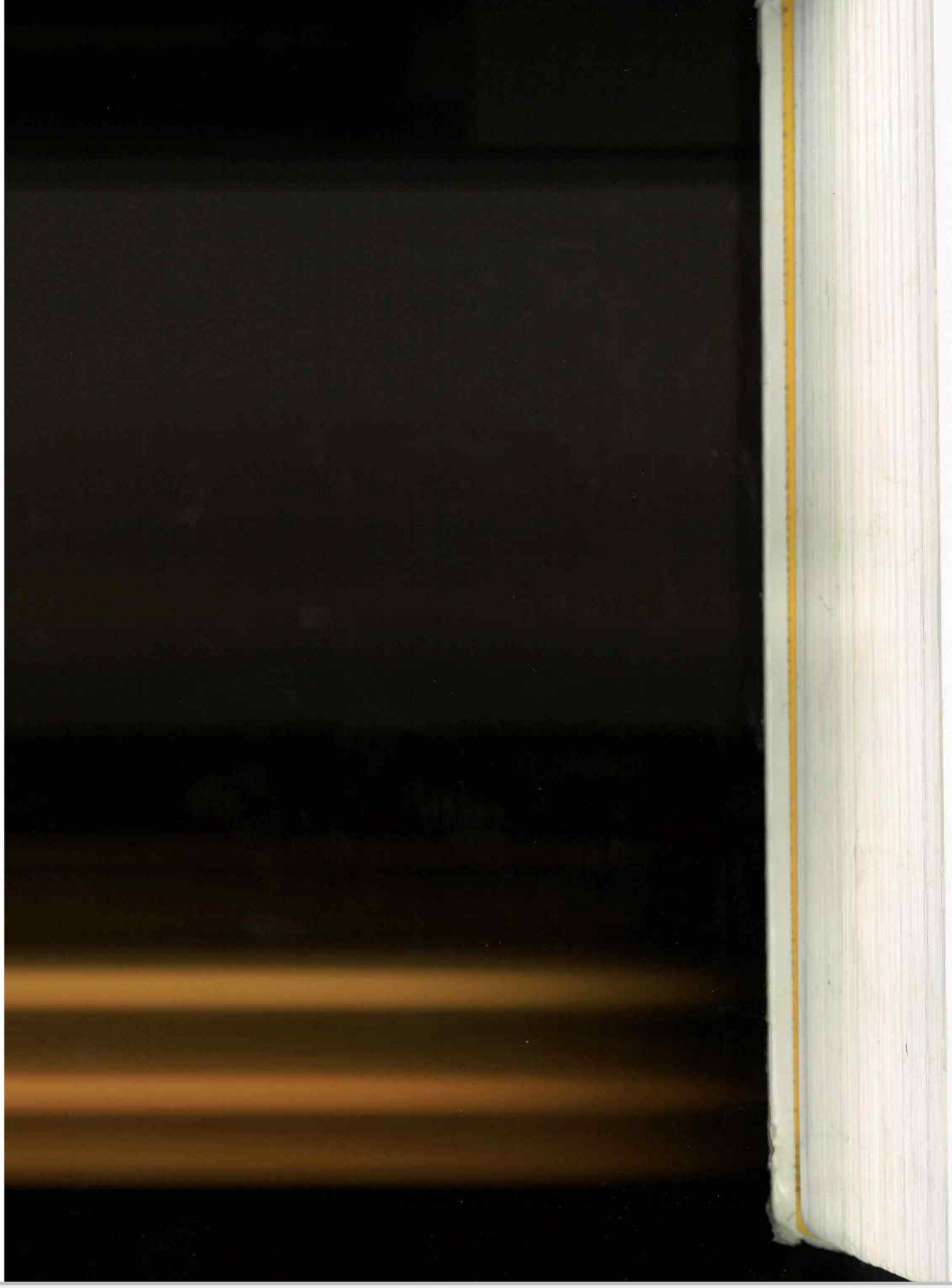
(b) $\text{Acetoacetate} + \text{NADH} + H^+ \longrightarrow \beta\text{-hydroxybutyrate} + NAD^+$

(c) $\text{Pyruvate} + \text{NADH} + H^+ \longrightarrow \text{lactate} + NAD^+$

(d) $\text{Pyruvate} + \beta\text{-hydroxybutyrate} \longrightarrow \text{lactate} + \text{acetoacetate}$

(e) $\text{Malate} + \text{pyruvate} \longrightarrow \text{oxaloacetate} + \text{lactate}$

(f) $\text{Acetaldehyde} + \text{succinate} \longrightarrow \text{ethanol} + \text{fumarate}$



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