

Lincoln College Biochemistry Tutorials

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1st years, Hilary Term, Tutorial 2

Title: Biophysical Chemistry – Thermodynamics (Lincoln)

You should ensure you have notes on the following areas:

Basic chemical thermodynamics:

1. Basic Definitions. 1st Law of thermodynamics.
2. 2nd Law and entropy. Free energy and equilibria. Single component systems.
3. Chemical potential and multiple component systems.
4. Determining thermodynamic functions. Multiple step processes.

Solution thermodynamics:

1. Behaviour of ideal solutions (and solvents). Definition of ideality. Solvent in dilute solutions, colligative properties, osmotic pressure.
2. Behaviour of non-ideal solutions (and solutes). Definition of non-ideality. Activities and activity coefficients.
3. Behaviour of ionic solutions I. Thermodynamics of hydration. Introduction to Debye-Hückel Theory.
4. Behaviour of ionic solutions II. Result of Debye-Hückel Theory, ionic strength. More concentrated ionic solutions.
5. Electrochemical potential: effect of an electric field on chemical potential, membrane potentials and Nernst equation for membranes, Oxidation-reduction reactions, thermodynamics of redox reactions.

References

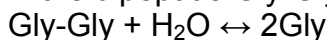
- Principles and Problems in Physical Chemistry for Biochemists, 3rd edition, N.C. Price, R.A. Dwek, R.G. Ratcliffe and M.R. Wormald, Oxford University Press -- the standard 'Oxford 1st year biochemists' text.
- Basic Chemical Thermodynamics, E.B. Smith, Oxford Chemistry Series, Oxford University Press --the standard 'Oxford 1st year chemists' text on thermodynamics -- slightly more advanced and very good.
- Physical Chemistry for the Biomedical Sciences, S.R. Logan, Taylor & Francis.
- Physical Chemistry for the Life Sciences, P.W. Atkins and J. de Paula, Oxford University Press --more simple version of the ubiquitous 'Physical Chemistry' -- highly recommended.
- Bioenergetics at a glance, D.A. Harris, Blackwell -- 1st few chapters give a good overview.
- Ions in solution (2): an introduction to electrochemistry, J. Robbins, pub. Oxford -- *the standard 'Oxford 1st year chemists' text on electrochemistry, again slightly more advanced and very good.*

Problems

All submitted material to be attached as one bundle from each separate student, to be clearly marked with the title of the tutorial, the date, the name of the student, and to clearly display "FAO Dr. Mark Leake, Clarendon Lab" on the first page. To be handed in to either the receptionist, or placed in the "L" pigeon-hole, of the Clarendon Laboratory, Dept of Physics by 12 noon the day before the tutorial.

1) State the first and second laws of thermodynamics and discuss their use in predicting whether a chemical reaction can occur spontaneously. [7]

Use the enthalpies of formation at pH 7 given below to calculate ΔH° for the hydrolysis of the amide bond in the dipeptide Gly-Gly. [6]



$$\Delta H^\circ_{\text{formation}}(\text{Gly-Gly}) \quad -747.7 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{formation}}(\text{Gly}) \quad -527.5 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{formation}}(\text{H}_2\text{O}) \quad -285.8 \text{ kJ mol}^{-1}$$

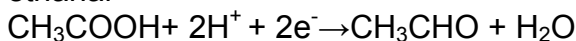
Comment of value of $\Delta H^\circ_{\text{hydrolysis}}(\text{Gly-Gly})$ that you have calculated in the light of the following average single bond dissociation enthalpies. [6]

Bond	Average dissociation enthalpy
C-N	+275 kJ mol ⁻¹
C-O	+330 kJ mol ⁻¹
H-N	+385 kJ mol ⁻¹
H-O	+455 kJ mol ⁻¹

Assuming that the $\Delta H^\circ_{\text{hydrolysis}}$ value that you have calculated for Gly-Gly is similar for all other dipeptide linkages, discuss the implications of this value for the stability of proteins in aqueous solution. [6]

2) What is meant by a *standard electrode potential*? Explain why a half-cell can have different standard electrode potentials in the normal and biochemical standard states. [5]

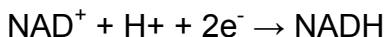
The standard electrode potential (E°) for the reduction of ethanoic acid to ethanal



is -0.185 V at 300K.

(i) Calculate the electrode potential for this half-cell in the biochemical standard state (E°).

(ii) The electrode potential in the biochemical standard state for the reduction of NAD^+ to NADH



is -0.32 V at 300K. Would the electrode potential for this half-cell vary more or less with pH than that for ethanoic acid/ethanal? Give your reasoning.

(iii) Calculate the equilibrium constant in the biochemical standard state (K') for the oxidation of ethanol by NAD^+ . [6]

(iv) What additional information would you need in order to be able to determine ΔH° and ΔS° for the oxidation of ethanal by NAD^+ ? [2]

3) What is the hydrophobic effect and how does it originate? How does the effect depend on temperature? [11]

At 303 K, ΔH° for the association of enzyme subunits to give catalytically active dimers was found to be $+16.8 \text{ kJ mol}^{-1}$. The value of ΔS° was $+58.6 \text{ kJ mol}^{-1}$.

Comment on the magnitude and signs of ΔH° and ΔS° . What does this indicate about the nature of the inter-subunit interactions? [6]

Would association be favoured at 303 K? [2]

Predict the effect the degree of association of

(a) a small rise or fall in temperature

(b) a large rise or fall in temperature [6]