Exam 2 SOLUTION KEY – Spring 2019

BCH 341 - Physical Chemistry with a Biological Focus
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February 5-6, 2019

DUE Thursday, Feb. 7, 2019 by 11:59 PM (UTC-7). Turn in completed exam as a single PDF document into the assignment link on ASU Canvas. Please make sure the completed exam is organized, self-contained and legible.

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To aid in the anonymous peer review process, you do NOT need to include your full name, just your first and last initials, and an email address for contact purposes. The exam consists of 8 numerical problems. The first 4 problems are worth 10 pts each and the last 4 problems are worth 15 pts each. Hence, the exam is worth a total of 100 points. You are required to explicitly show all equations, numerical calculations and associated units. All assumptions need to be clearly and concisely stated. If thermodynamic parameters are used, the citation, reference or link to where this thermodynamics data came from must be stated.

*** Prof. Mujica and Yarger made a video to further help students with the solutions associated with this exam. Please see biopchem.education for the associated link to the video.*

SOLUTION TO EXERCISE 1.

True or false

a. The entropy of an open system cannot decrease in a spontaneous process.

   T [✓ **F**]

   Comment: It is the total entropy of the universe, system plus environment, that cannot decrease in a spontaneous process.

b. Given that the equilibrium constant depends on the temperature only, the composition of the equilibrium mixture in a gas reaction is insensitive to the external pressure.

   T [✓ **F**]

   Comment: The composition of the equilibrium mixture is, in general, sensitive to the external pressure. It changes in a way that compensates the change in pressure to keep the equilibrium constant invariant. This is in agreement with the Le Chatelier's principle.

c. A change in external pressure has no effect on the melting temperature of a pure substance.

   T [✓ **F**]

   Comment: The chemical potential of a phase depends on the pressure; as a consequence, the solid-liquid equilibrium will be affected.

d. A chemical reaction for which the standard reaction Gibbs energy is positive is impossible.

   T [✓ F]

   Comment: The condition for a chemical reaction to be spontaneous is that the reaction Gibbs energy, not the standard reaction Gibbs energy, should be negative. One could also add that, in general, there are no impossible reactions. Once can always compensate a negative free energy changing the conditions.

2. A very interesting comparison is that between a thermal engine and living systems, say us. Thermal engines operate under a temperature gradient, as a vapor locomotive, whereas we are essentially isothermal systems. Also, the second law of thermodynamics establishes that the entropy of the universe increases in any spontaneous process, eventually leading to equilibrium.

Discuss the following aspects in qualitative terms:

a. What is the source of useful work in biological systems?
b. How do we maintain steady state?
c. Are there biological processes that occur reducing entropy? If the answer is yes, how do we reconcile this fact with the second law of thermodynamics?

SOLUTION TO EXERCISE 2.

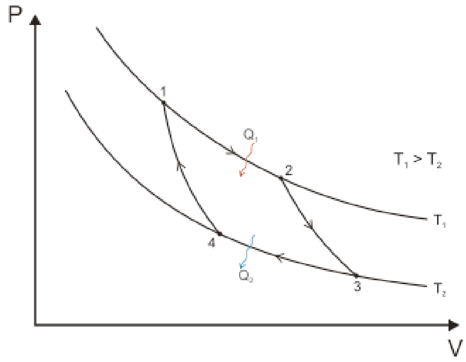
a. The source of useful work in biological systems is primarily chemical and electrochemical transformations, occurring essentially under isothermal conditions. This requires the existence of chemical potential gradients originated from concentration and electric potential differences.

b. Steady state is maintained by absorbing food and excreting residues and chemical substances, which are produced in the process of transforming food into nutrients. This steady state is very different from true equilibrium, even though the concentrations of important molecules are kept nearly constant.

c. Many biological processes occur reducing entropy. This does not constitute a violation of the second law of thermodynamics, because the law requires the entropy of the universe, i.e., system and environment, to increase. Biological systems are neither closed nor isolated, therefore entropy can be reduced within the system at the expense of increasing it in the environment.

3. The figure below corresponds to a plot of a Carnot cycle consisting of the following operations with a gas as operating substance.

- Path 1->2. Reversible isothermal expansion.
- Path 2->3. Reversible adiabatic expansion.
- Path 3->4. Reversible isothermal compression.
- Path 4->1. Reversible adiabatic compression.



(i) Draw a graph of entropy against temperature for the entire cycle.
(ii) What is the entropy change in the cycle, for the system? And for the surroundings?

SOLUTION TO EXERCISE 3

The Carnot cycle consists of:

- Two isothermal steps (1->2) at T_1 and (3->4) at T_2 where the temperature is held constant. For these steps, we have

$$\Delta S_{1\to 2} = \frac{Q_1}{T_1}$$

$$\Delta S_{3\to 4} = \frac{Q_2}{T_2}$$

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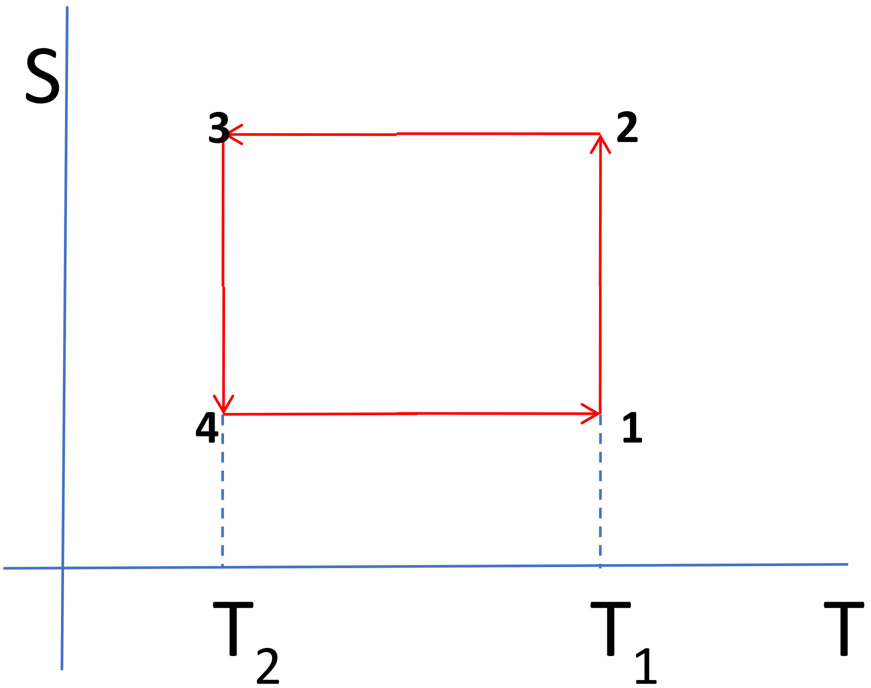
- Two isentropic steps (2->3) and (4->1) where the entropy does not change. This is so because these two steps are reversible and adiabatic, and therefore

$$\Delta S_{2\to 3} = 0$$

$$\Delta S_{4\to 1} = 0$$

A graph of S vs T for the Carnot cycle would then be

S-T diagram for a Carnot cycle



(iii) The total entropy change of the system for the whole cycle must be zero because the entropy is a state function. For each step, the entropy change in the surroundings must be equal to the entropy change in the system, because each step in a Carnot cycle is reversible.

$$\Delta S_{cycle} = \underbrace{\Delta S_{1\to 2}}_{=\frac{Q_1}{T_1}} + \underbrace{\Delta S_{2\to 3}}_{=0} + \underbrace{\Delta S_{3\to 4}}_{=\frac{Q_2}{T_2}} + \underbrace{\Delta S_{4\to 1}}_{=0}$$

4. The molar mass of an enzyme was determined by dissolving it in water measuring the osmotic pressure at 20 ºC and extrapolating the data to zero concentration. The following data for the height of the column, containing the solution, and the concentration, were used:

c/ mg cm^{-3}	3.221	4.618	5.112	6.722
h/cm	5.746	8.238	9.119	11.990

Calculate the molar mass of the enzyme. *Hint*: Begin by expressing the equation given the osmotic pressure in terms of the height of the solution, by using $\Pi=\rho gh$; take $\rho=1.000$ g cm^{-3}.

SOLUTION TO EXERCISE 4

We start by considering vant' Hoff for the osmotic pressure: (Section 3.10 Atkins textbook)

$$\Pi V = n_B RT$$

$$\Pi = [B]RT \qquad (4\text{-}1)$$

where $[B]=n_B/RT$ is the molar concentration of the solute. This equation applies only to solutions that are sufficiently diluted to behave as ideal-dilute solutions.

Biological macromolecules produce non-ideal solutions. We have then to consider the so-called osmotic virial expansion for the osmotic pressure, that includes non-linear terms in the concentration of the solute. The simplest such expansion is:

$$\Pi = [B]RT\{1 + B[B] + \ldots\} \qquad (4\text{-}2)$$

where B is an empirical coefficient. This equation can be rearranged into the form

$$\frac{\Pi}{[B]} = RT\{1 + B[B] + \ldots\} \quad (4\text{-}3)$$

Hence a plot of $\Pi/_{[B]}$ vs [B] gives a straight line.

Equation (4-3) is the starting point to solve exercise 4. To express it in terms of concentrations we write the mass concentration $c_B=m_B/V$ as

$$c_B = \frac{m_B}{V} = \frac{m_B}{n_B} x \frac{n_B}{V} = M[B]$$

where M is the molar mass of the solute, so that $[B]=c_B/M$. With this substitution, equation (4-3) becomes

$$\frac{\Pi}{c_B} = \frac{RT}{M} + \left(\frac{BRT}{M^2}\right) c_B \; + \ldots \qquad (4\text{-}4)$$

indicating that a plot of $\Pi/_{c_B}$ against c_B results in a straight line with intercept equal to RT/M. This plot allows us to find the molar mass of the solute.

To solve the exercise, first we need to express the values of the osmotic pressure in terms of the height of the column as $\Pi = \rho g h$

Then

$$\frac{h}{c_B} = \frac{\Pi}{\rho g c_B} = \frac{RT}{\rho g M} + \left(\frac{RTB}{\rho g M^2}\right) c_B \quad + \ldots \tag{4-5}$$

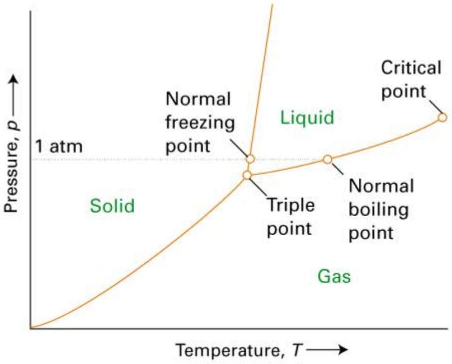
indicating that a plot of h/c_B has an intercept equal to $\frac{RT}{\rho g M}$, from which we can determine M. From the table in the statement of the problem we can obtain:

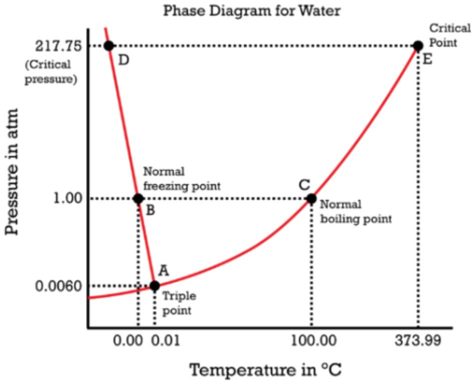
c/ mg cm^{-3}	3.221	4.618	5.112	6.722
h/ cm	5.746	8.238	9.119	11.990
h/c /mg^{-1} cm^4	1.784	1.783	1.784	1.784

Inspection of this table reveals that the second term in equation (4-5) is zero, because the value of h/c is constant, i.e. B=0. That is, the solution of the enzyme behaves ideally. Hence, we determine the molar mass directly as:

$$M = \frac{RT}{\rho g \; x \left({}^{h}/{}_{c_B}\right)} = 13.93 \; kg \; mol^{-1}$$

5. The figure below to the left shows a schematic plot of the phase diagram for a typical pure substance, and the one to the right displays the phase diagram of water.





There is a fundamental difference between the two diagrams, namely the slope of the solid-liquid equilibrium curve, which is negative for water and positive for most substances.

(i) Use Clausius-Clapeyron equation to explain the origin of this difference.
(ii) Use this result to explain the behavior of ice under pressure. How is this relevant for ice-skaters?
(iii) Analyze the importance of this difference for the sustainability of life in our planet. In particular, discuss the behavior of water under freezing conditions on lakes and oceans. What would happen to fish during wintertime if the solid-liquid phase line for water had positive slope?

SOLUTION TO EXERCISE 5.

(i) Clapeyron equation gives the slope of a phase transition curve. The simplest way to derive it is to consider the phase equilibrium condition for two phases, α, and β,

$$d\mu_\alpha = d\mu_\beta \qquad \text{(5i-1)}$$

where μ, the chemical potential, is equal to the molar Gibbs free energy, and

$$d\mu = V_m dP - S_m dT = \overline{V}dP - \overline{S}dP \qquad \text{(5i-2)}$$

Equation (5i-1) leads to

$$\begin{gathered}\overline{V}_\alpha dP - \overline{S}_\alpha dT = \overline{V}_\beta dP - \overline{S}_\beta dT \\ \left(\overline{S}_\beta - \overline{S}_\alpha\right)dT = \left(\overline{V}_\beta - \overline{V}_\alpha\right)dT \\ \triangle\,\overline{S}_{\alpha\beta}dT = \triangle\,\overline{V}_{\alpha\beta}dP\end{gathered} \qquad \text{(5i-3)}$$

For the particular case of the solid-liquid phase transition, we then have

$$\frac{dP}{dT} = \frac{\Delta \bar{S}_f}{\Delta \bar{V}_f}$$

While the change in molar entropy for the solid-liquid transition is always positive, the change in molar volume depends on the substance. For most substances, the latter is positive, but water is an exception because at the normal transition temperature of approximately 0 ^{o}C, water expands when ice is formed, leading to the usual consequence that ice is less dense than liquid water, and hence it floats.

(ii) The result discussed in (i) implies that the melting point of ice is reduced under pressure, which is important both for ice skating and also to explain the advance of glaciers: when a large rock is encountered the interfacial pressure increases leading to ice melting and the liquid water surrounds the rock instead of pushing it along.

(iii) The unusual behavior of water, has enormous consequences for life in our planet. Because ice floats on water, oceans and lakes do not freeze from the bottom, which would kill all life in the water. The layer of ice actually protects the water underneath from further freezing.

6. Being able to control the pH, is essential in biochemical experiments.

(i) Predict the pH region in which each of the following buffers will be effective, assuming equal molar concentrations of the acid and its conjugate base: (a) sodium lactate and lactic acid. (b) sodium benzoate and benzoic acid. (c) hydroxylamine and hydroxyl ammonium chloride.

(ii) Draw a plot of the pH curve of a solution containing 0.10 M $NaCH_3CO_2$(aq) and a variable amount of acetic acid.

SOLUTION TO EXERCISE 6

(i) To solve this problem, we need the values of some acidity and basicity constants.

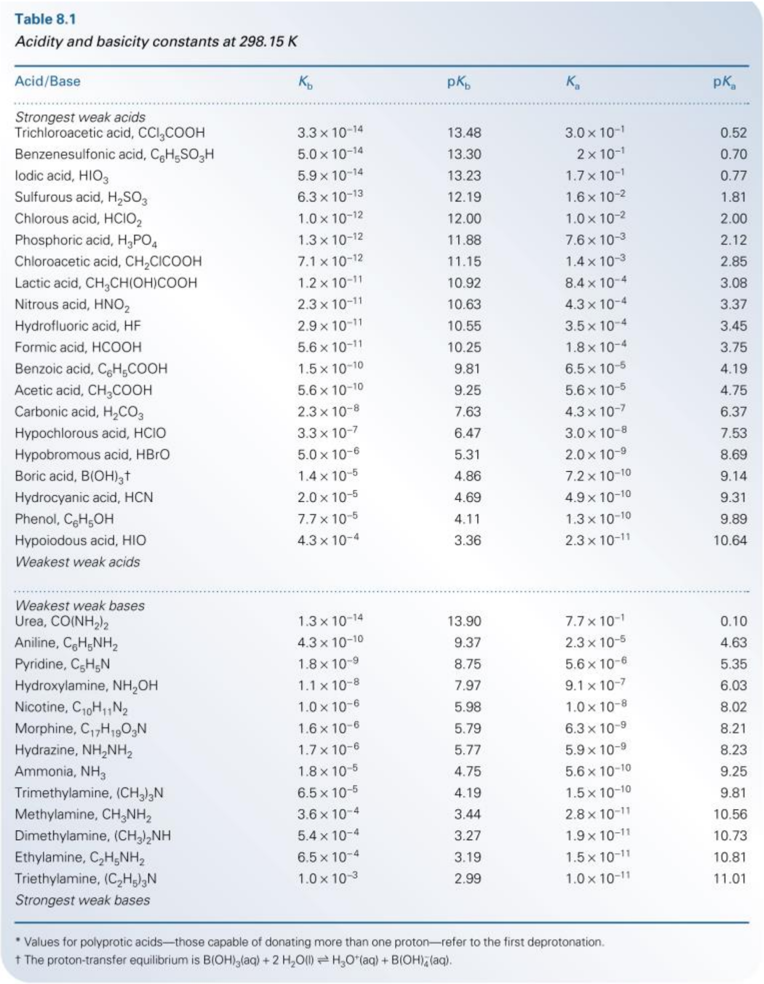


Table 8.1

Acidity and basicity constants at 298.15 K

Acid/Base	K_b	pK_b	K_a	pK_a
Strongest weak acids				
Trichloroacetic acid, CCl_3COOH	3.3×10^{-14}	13.48	3.0×10^{-1}	0.52
Benzenesulfonic acid, $C_6H_5SO_3H$	5.0×10^{-14}	13.30	2×10^{-1}	0.70
Iodic acid, HIO_3	5.9×10^{-14}	13.23	1.7×10^{-1}	0.77
Sulfurous acid, H_2SO_3	6.3×10^{-13}	12.19	1.6×10^{-2}	1.81
Chlorous acid, $HClO_2$	1.0×10^{-12}	12.00	1.0×10^{-2}	2.00
Phosphoric acid, H_3PO_4	1.3×10^{-12}	11.88	7.6×10^{-3}	2.12
Chloroacetic acid, $CH_2ClCOOH$	7.1×10^{-12}	11.15	1.4×10^{-3}	2.85
Lactic acid, $CH_3CH(OH)COOH$	1.2×10^{-11}	10.92	8.4×10^{-4}	3.08
Nitrous acid, HNO_2	2.3×10^{-11}	10.63	4.3×10^{-4}	3.37
Hydrofluoric acid, HF	2.9×10^{-11}	10.55	3.5×10^{-4}	3.45
Formic acid, HCOOH	5.6×10^{-11}	10.25	1.8×10^{-4}	3.75
Benzoic acid, C_6H_5COOH	1.5×10^{-10}	9.81	6.5×10^{-5}	4.19
Acetic acid, CH_3COOH	5.6×10^{-10}	9.25	5.6×10^{-5}	4.75
Carbonic acid, H_2CO_3	2.3×10^{-8}	7.63	4.3×10^{-7}	6.37
Hypochlorous acid, HClO	3.3×10^{-7}	6.47	3.0×10^{-8}	7.53
Hypobromous acid, HBrO	5.0×10^{-6}	5.31	2.0×10^{-9}	8.69
Boric acid, $B(OH)_3$†	1.4×10^{-5}	4.86	7.2×10^{-10}	9.14
Hydrocyanic acid, HCN	2.0×10^{-5}	4.69	4.9×10^{-10}	9.31
Phenol, C_6H_5OH	7.7×10^{-5}	4.11	1.3×10^{-10}	9.89
Hypoiodous acid, HIO	4.3×10^{-4}	3.36	2.3×10^{-11}	10.64
Weakest weak acids				
Weakest weak bases				
Urea, $CO(NH_2)_2$	1.3×10^{-14}	13.90	7.7×10^{-1}	0.10
Aniline, $C_6H_5NH_2$	4.3×10^{-10}	9.37	2.3×10^{-5}	4.63
Pyridine, C_5H_5N	1.8×10^{-9}	8.75	5.6×10^{-6}	5.35
Hydroxylamine, NH_2OH	1.1×10^{-8}	7.97	9.1×10^{-7}	6.03
Nicotine, $C_{10}H_{11}N_2$	1.0×10^{-6}	5.98	1.0×10^{-8}	8.02
Morphine, $C_{17}H_{19}O_3N$	1.6×10^{-6}	5.79	6.3×10^{-9}	8.21
Hydrazine, NH_2NH_2	1.7×10^{-6}	5.77	5.9×10^{-9}	8.23
Ammonia, NH_3	1.8×10^{-5}	4.75	5.6×10^{-10}	9.25
Trimethylamine, $(CH_3)_3N$	6.5×10^{-5}	4.19	1.5×10^{-10}	9.81
Methylamine, CH_3NH_2	3.6×10^{-4}	3.44	2.8×10^{-11}	10.56
Dimethylamine, $(CH_3)_2NH$	5.4×10^{-4}	3.27	1.9×10^{-11}	10.73
Ethylamine, $C_2H_5NH_2$	6.5×10^{-4}	3.19	1.5×10^{-11}	10.81
Triethylamine, $(C_2H_5)_3N$	1.0×10^{-3}	2.99	1.0×10^{-11}	11.01
Strongest weak bases				

* Values for polyprotic acids—those capable of donating more than one proton—refer to the first deprotonation.

† The proton-transfer equilibrium is $B(OH)_3(aq) + 2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + B(OH)_4^-(aq)$.

Henderson-Hasselbalch equation reads

$$pH = pK_a - \log\frac{[acid]}{[base]}$$

For equal concentrations of the acid and the base, the resulting pH is approximately equal to pK_a. This relation allows us to predict the pH region in which each of the buffers will be effective. A typical rule of thumb is that the effective range of a buffer is roughly within plus or minus one pH unit of the pK_a of the acid, but other approximate rules are equally acceptable. The following table summarizes the results

Buffer system	**pKa**	**Effective pH buffer range**
Lactate/lactic acid	3.08	2-4
Benzoate/benzoic acid	4.19	3-5
NH_2OH/ $^+NH_3OH$	6.03	5-7

(ii) Draw a plot of the pH curve of a solution containing 0.10 M $NaCH_3CO_2(aq)$ and a variable amount of acetic acid.

The initial pH can be calculated directly from the equilibrium constant for the reaction, assuming that the concentration of $CH_3CO_2^-$ remains approximately constant.

$$CH_3CO_2^- + H_2O \rightleftharpoons \mathrm{CH_3COOH} + \mathrm{OH^-}$$

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3CO_2^-]} = \frac{x^2}{0.10} = 5.6\ x\ 10^{-10}$$

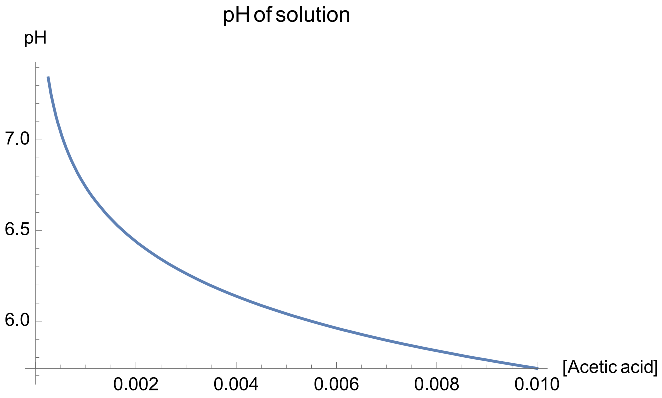
From which we can obtain,

$$x = [OH^-] = 7.5\ x\ 10^{-6}, pOH = 5.12, pH = 8.88$$

We can then use Henderson-Hasselbalch equation to calculate the values of pH at other concentrations of CH_3COOH.

$$pH = 4.74 - \log\frac{[acid]}{[base]} = 4.74 - \log\frac{[CH_3COOH]}{0.10\ mol\ dm^{-3}}$$

A plot of this equation is given below



7. The equilibrium constant of the reaction 2 $C_3H_6(g) \rightleftharpoons C_2H_4(g) + C_4H_8(g)$ is found to fit the expression

$$\ln K(T) = -1.04 - \frac{1.088\ \mathrm{K}}{T} + \frac{1.51\ x\ 10^5\ \mathrm{K}^2}{T^2}$$

Between 300 K and 600 K. Calculate the standard reaction energy and standard reaction entropy at 400 K.

SOLUTION TO EXERCISE 7

The starting point is Gibbs equation for the reaction energy

$$\Delta_r G^o = \Delta_r H^o - T\Delta_r S^o \qquad (7-1)$$

and the equation connecting the equilibrium constant to the reaction energy

$$\Delta_r G^o = -RT\ln K \qquad (7-2)$$

We can combine equations (7-1) and (7-2) to obtain:

$$\ln K = -\frac{\Delta_r G^o}{RT} = -\frac{\Delta_r H^o}{RT} + \frac{\Delta_r S^o}{R} \qquad (7-3)$$

Assuming that the standard reaction enthalpy and entropy are independent of the temperature over the range of interest, we can write equation (7-3) for a different temperature T' as

$$\ln K' = -\frac{\Delta_r G^o}{RT'} = -\frac{\Delta_r H^o}{RT'} + \frac{\Delta_r S^o}{R} \qquad (7-4)$$

and subtracting (7-3) from (7-4) we obtain van't Hoff equation

$$\ln K' - \ln K = \frac{\Delta_r H^o}{R}\left(\frac{1}{T} - \frac{1}{T'}\right) \qquad (7-5)$$

We can now choose any two temperatures in the range specific by the problem, say T=390 K, T'=410 K and the equation for K(T)

$$\ln K = -1.04 - \frac{1.088\ K}{T} + \frac{1.51\ x\ 10^5\ K^2}{T^2}$$

to obtain ln K(390)=-2.84, and ln K(410)=-2.80, We then substitute these numbers into van't Hoff equation to obtain $\Delta_r H^o = 2.66\ kJ\ mol^{-1}$.

A simple substitution in equation (7-2) leads to $\Delta_r G^o = 9.36\ kJ\ mol^{-1}$, and finally, from equation (7-1) we find

$\Delta_r S^o = \frac{\Delta_r H^o - \Delta_r G^o}{T} = -16.8\, J\ \mathrm{K}^{-1} mol^{-1}$.

8. Under certain stress conditions, such as viral infections or hypoxia, plants have been shown to have an intercellular pH increase of about 0.1 pH. Suppose this pH change also occurs in the mitochondrial intermembrane space. How much ATP can now be synthetized for the transport of 2 mol H^+, assuming no other changes occur?

SOLUTION TO EXERCISE 8

To solve this problem, we start by reminding that according to the chemiosmotic theory H^+-ATPases use the energy stored in a transmembrane proton gradient to synthetize ATP from ADP. The normal pH difference across the inner mitochondrial membrane is ΔpH=-1.4, and the membrane potential difference is $\Delta\phi$=70 mV.

The Gibbs energy available for phosphorylation according to this theory is (Atkins (5.20))

$$\Delta G_m = RT\ln\frac{[H^+]_{in}}{[H^+]_{out}} + F\Delta\phi = F\Delta\phi - (RT\ln 10)\Delta pH$$

where $\Delta pH = pH_{in} - pH_{out}$.

Also, according to the information in Atkins textbook 31 kJ mol^{-1} is needed for phosphorylation, which means that at least 2 mol of H^+ must flow through the membrane for the phosphorylation of 1 mol ADP.

According to the statement of the problem there is a pH increase of about 0.1 pH that occurs in the mitochondrial intermembrane space. Thus $\Delta pH = pH_{in} - pH_{out}$=-1.3.

Hence,

$$\Delta G_m = F\Delta\phi - (RT\ln 10)\Delta pH = 14.5\ kJ\ mol^{-1}$$

For 2 mol H^+, $\Delta G = (2\ mol)x(14.5\ kJ\ mol^{-1}) = 29\ kJ$

Since 31 kJ mol^{-1} is needed for the synthesis of ATP, under the described stress conditions the amount of ATP that could be synthetized is

$$\frac{29\ kJ}{31\ kJ\ mol^{-1}} = 0.93\ mol$$