

A-166 0 °C

Ice is at equilibrium with water at this temperature ($\Delta G = 0$).

- R
- a) $\Delta G = \Delta H - T\Delta S$
 - b) $\Delta G = \sum nG_p - \sum nG_r$
 - c) $\Delta G_f^\circ = G^\circ$
 - d) ΔG_f° for an element = 0
 - e) $\Delta G^\circ = \sum n\Delta G_f^\circ(p) - \sum n\Delta G_f^\circ(r)$
 - f) Superscript indicates standard state, 101.3 kN m⁻² (1 atm) pressure and 25 °C.
 - g) The sign of ΔG is the criterion of spontaneity for a reaction or process.
- $\Delta G = -$ (spontaneous)
 $\Delta G = +$ (spontaneous in reverse direction)
 $\Delta G = 0$ (equilibrium; reaction can go in either direction)

PART II: Equilibrium and Its Relationship to Thermodynamic Quantities

S-1 In the previous section criteria of spontaneity were developed for chemical reactions. The criteria were based on the calculation of ΔG° for the reaction from ΔH° and ΔS° . If the sign of ΔG° was negative, the reaction was said to be spontaneous. The ΔG° value corresponds to a reaction where all species (both reactants and products) are in their standard state, meaning 101.3 kN m⁻² pressure for gases, pure liquids and pure solids for condensed phases, and one molar (1.0 mol dm⁻³) solutions for solutes. Reactions under these conditions are not easy to achieve. A more common situation is one in which reactants are mixed and the reaction is allowed to proceed. When standard conditions are not used, important questions which need to be considered are

- a) What effect will a change in concentration have on the free energy change and consequently the spontaneity of the reaction?
- b) How far will the reaction proceed?

The variation in free energy, G , with activity, a , is expressed in the equation

$$G = nG^\circ + nRT 2.3 \log a$$

where G° is the standard free energy for one mole and n is the number of moles.

Q-1 The relationship between activity and concentration is expressed as

$$a = \gamma \frac{[c]}{[c^\circ]}$$

where $[c]$ is the concentration in mol dm⁻³, $[c^\circ]$ is the concentration of the standard state in mol dm⁻³, and γ is the activity coefficient which accounts for any deviation from ideal behavior. Show that for one mol dm⁻³ ideal solution, the free energy per mole is equal to the standard free energy G° . The standard state concentration is 1.0 mol dm⁻³.

For ideal solution $\gamma = 1$

A-1 $\gamma = 1$ ideal
 $[c^\circ] = 1.0 \text{ mol dm}^{-3}$ (standard state)
 $[c] = 1.0 \text{ mol dm}^{-3}$
 $n = 1$
 $G = G^\circ + RT 2.3 \log \frac{[c]}{[c^\circ]}$
 $G = G^\circ + RT 2.3 \log \frac{[1]}{[1]}$
 $G = G^\circ$

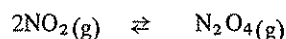
Q-2 The relationship between activity and pressure is expressed as

$$a = \gamma \frac{P}{P^\circ}$$

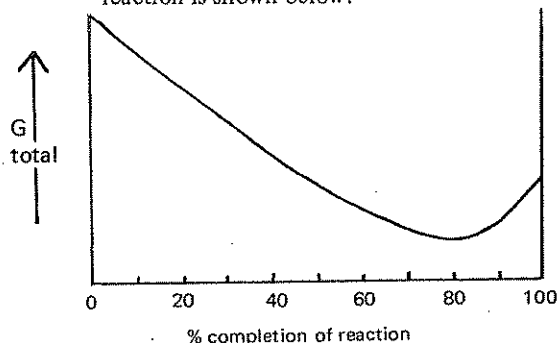
where P is the pressure in kN m^{-2} , P° is the pressure of the standard state, and γ has the same meaning as before. Show that for one mole of ideal gas at 101.3 kN m^{-2} the free energy is equal to the standard free energy G°

A-2 $\gamma = 1$ ideal
 $P = 101.3 \text{ kN m}^{-2}$
 $P^\circ = 101.3 \text{ kN m}^{-2}$ (standard state)
 $n = 1$
 $G = G^\circ + RT 2.3 \log \frac{P}{P^\circ}$
 $G = G^\circ + RT 2.3 \log \frac{101.3 \text{ kN m}^{-2}}{101.3 \text{ kN m}^{-2}}$
 $G = G^\circ$

Q-3 Consider the reaction for the dimerization of NO_2 .



The total free energy at any time during the reaction is the sum of the free energy of NO_2 and N_2O_4 . The total free energy as a function of the completion of the reaction is shown below.



How does the slope of the line vary as the % completion of the reaction increases?

A-3 In going from 0% to 100% of completion the slope decreases, goes to zero and then increases.

Q-4 What does a decrease in the slope indicate about the change in free energy.

A-4 The free energy change is negative.

Q-5 The change in free energy, ΔG , is expressed as

$$\Delta G = G_{\text{total}} - G_{\text{total}}$$

(final state) (initial state)

What is the sign of the free energy change in going from 0% completion to 50% completion for the reaction in Q-3? Would this be a spontaneous change?

A-5 Negative. This would be a spontaneous change.

Q-6 Would the change from 50% completion to 70% completion be a spontaneous reaction? Why?

A-6	Yes. The free energy decreases (ΔG negative).	Q-7	Would the change from 80% total completion to 100% completion be spontaneous? Why?
A-7	No. The free energy increases (ΔG = positive).	Q-8	A process will take place as long as the total free energy decreases. According to the graph in Q-3, when will the reaction stop?
A-8	When the per cent of total reaction reaches 80%.	Q-9	The reaction of NO_2 going to N_2O_4 doesn't really stop at a per cent completion equal to 80%. Rather, at 80% completion the rate at which NO_2 reacts to form N_2O_4 is equal to the rate at which N_2O_4 breaks down to form NO_2 . Consequently, the concentration or partial pressures of N_2O_4 and NO_2 will not change. This is called an <u>equilibrium</u> state. What is the slope of the curve given in Q-3 at the equilibrium point? What is the change in G_{total} ?
A-9	The slope is zero. $\Delta G_{\text{total}} = 0$. The total free energy reaches a minimum.	Q-10	If any further reaction occurred in either direction from the equilibrium point, what would have to be the sign of the total free energy change? Would this be a spontaneous change?
A-10	ΔG = positive. This would not be a spontaneous change.	Q-11	The ΔG° value for the reaction $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ is -4.8 kJ mol^{-1} . Does this mean that if one were to start with pure N_2O_4 , no NO_2 would form? Explain.
A-11	The ΔG° value is the change in free energy for the reactants and products in their standard state. If one started with pure N_2O_4 , it would break down into NO_2 until the total free energy reached a minimum.	Q-12	To take into account the variation in free energy of a substance with a variation in concentration or partial pressure, the equation given in S-1 must be used. This will allow for the calculation of the free energy change for a reaction under any conditions. Calculate a general expression for the free energy change, ΔG , for the reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$ in terms of ΔG° and activities. $\Delta G = G_{\text{D}} + G_{\text{C}} - G_{\text{A}} - G_{\text{B}}$

A-12 $\Delta G = G_D + G_C - G_A - G_B$

$$G_D = dG_D^\circ + dRT \, 2.3 \log a_D$$

$$G_C = cG_C^\circ + cRT \, 2.3 \log a_C$$

$$G_B = bG_B^\circ + bRT \, 2.3 \log a_B$$

$$G_A = aG_A^\circ + aRT \, 2.3 \log a_A$$

$$\Delta G = dG_A^\circ + cG_C^\circ - bG_B^\circ - aG_A^\circ +$$

$$dRT \, 2.3 \log a_D + cRT \, 2.3 \log a_C$$

$$-bRT \, 2.3 \log a_B - aRT \, 2.3 \log a_A$$

$$\Delta G^\circ = dG_D^\circ + cG_C^\circ - bG_B^\circ - aG_A^\circ$$

$dRT \, 2.3 \log a_D$ can be written as

$$RT \, 2.3 \log a_D^d$$

Therefore,

$$\Delta G = \Delta G^\circ + RT \, 2.3 \log \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

This equation applies generally to any conditions.

Q-13 What is the value for ΔG in the equation of A-12 when a reaction attains equilibrium?

A-13 $\Delta G = 0$

Q-14 Solve the equation derived in A-12 for ΔG° when a reaction is at equilibrium.

A-14 $\Delta G = \Delta G^\circ + RT \, 2.3 \log \frac{a_C^c a_D^d}{a_A^a a_B^b}$

At equilibrium $\Delta G = 0$

$$\Delta G^\circ = -RT \, 2.3 \log \left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right)_{\text{equilibrium activities}}$$

Q-15 Since at a given temperature ΔG° is a constant, the quantity inside the log term has to be a constant. This constant is called the thermodynamic equilibrium constant, K_{th} . Write the equation for ΔG° in terms of K_{th} . Write the expression for K_{th} in terms of activities of reactants and products.

A-15 $\Delta G^\circ = -RT \, 2.3 \log K_{th}$

Q-16 Write an expression for the thermodynamic equilibrium constant in terms of activity for the reaction

$$K_{th} = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

where the activities are those at equilibrium.



A-16

$$K_{th} = \frac{a_{N_2O_4}}{a_{NO_2}^2}$$

Q-17

From a knowledge of the ΔG° for the reaction given in Q-16, calculate the value of K_{th} for 298 K.

$$\Delta G^\circ \text{ for the reaction is } -4.8 \text{ kJ mol}^{-1}$$

$$R = 8.31 \text{ J K}^{-1}$$

A-17

$$\Delta G^\circ = -4.8 \text{ kJ}$$

$$\Delta G^\circ = -RT \cdot 2.3 \log K_{th}$$

$$R = 8.31 \text{ J K}^{-1}$$

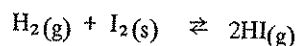
$$\frac{1000 \text{ J}}{1 \text{ kJ}} (-4.8 \text{ kJ}) = (-8.31 \text{ J K}^{-1}) (298 \text{ K}) (2.3) \log K_{th}$$

$$\log K_{th} = 0.84$$

$$K_{th} = 6.9$$

Q-18

Calculate ΔG° for the reaction



at a pressure of 101.3 kN m^{-2} and a temperature of 298 K.

(See Table III, page 376).

A-18

$$\Delta G_f^\circ(H_2)_g = 0$$

$$\Delta G_f^\circ(I_2)_s = 0$$

$$\Delta G_f^\circ(HI)_g = 1.6 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ = 2\Delta G_f^\circ(HI) - \Delta G_f^\circ(H_2) - \Delta G_f^\circ(I_2)$$

$$\Delta G^\circ = 3.2 \text{ kJ}$$

Q-19

Calculate K_{th} at 298 K for the reaction given in Q-18.

A-19

$$\Delta G^\circ = 3.2 \text{ kJ}$$

$$\Delta G^\circ = -RT \cdot 2.3 \log K_{th}$$

$$R = 8.31 \text{ J K}^{-1}$$

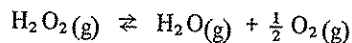
$$\left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right) 3.2 \text{ kJ} = (-8.31 \text{ J K}^{-1}) (298 \text{ K}) (2.3) \log K_{th}$$

$$\log K_{th} = -0.56$$

$$K_{th} = 0.27$$

Q-20

For the decomposition of gaseous hydrogen peroxide according to the reaction



$\Delta G^\circ = -125 \text{ kJ}$. What is the value of the thermodynamic equilibrium constant for this reaction at 298 K?

A-20 $\Delta G^\circ = -RT \, 2.3 \log K_{th}$

$$\log K_{th} = \frac{(-125 \text{ kJ}) \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right)}{(8.31 \text{ J K}^{-1}) (2.3) (298 \text{ K})}$$

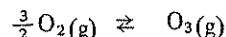
$$= 21.9$$

$$K_{th} = 7.9 \times 10^{21}$$

A-21 The reaction goes essentially to completion. The activity of the products is a lot greater than the activity of the reactant.

Q-21 A very negative ΔG° (-50 kJ) corresponds to a large K_{th} value. What does this mean about the extent to which the reaction takes place?

Q-22 When gaseous ozone, O_3 , is formed from molecular oxygen by the reaction



The standard free energy change is +164 kJ. What is the thermodynamic equilibrium constant of the reaction at 298 K?

A-22 $\Delta G^\circ = -(2.3) RT \log K_{th}$

$$\log K_{th} = \frac{-(164 \text{ kJ}) \left(\frac{1000 \text{ J}}{1 \text{ kJ}} \right)}{(8.31 \text{ J K}^{-1}) (2.3) (298 \text{ K})}$$

$$= -28.8$$

$$K_{th} = 2.0 \times 10^{-29}$$

Q-23 A very positive ΔG° corresponds to a very small K_{th} value. What does this mean about the extent to which the reaction takes place?

A-23 The reaction from right to left takes place to a very small extent. The reaction in the reverse direction would go almost to completion.

Q-24 From the relationship given between activity and concentration in Q-1, express the thermodynamic equilibrium constant from A-15 in terms of concentration.

A-24 $a = \gamma \frac{[c]}{[c^\circ]}$ (Q-1)

$$K_{th} = \frac{a_C^c a_D^d}{a_A^a a_B^b} \quad (\text{A-15})$$

$$a_C^c = \gamma_C^c \frac{[C]^c}{[C^\circ]^c}$$

$$a_D^d = \gamma_D^d \frac{[D]^d}{[D^\circ]^d}$$

$$a_A^a = \gamma_A^a \frac{[A]^a}{[A^\circ]^a}$$

$$a_B^b = \gamma_B^b \frac{[B]^b}{[B^\circ]^b}$$

$$K_{th} = \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \frac{[C]^c [D]^d [A^\circ]^a [B^\circ]^b}{[C^\circ]^c [D^\circ]^d [A]^a [B]^b}$$

Q-25 Assuming that all the activity coefficients in A-24 are equal to unity (ideal solutions) and the standard states are 1 mol dm^{-3} , give the expression for K_{th} .

- A-25 When $\gamma = 1$ and all standard states are 1 mol dm^{-3}

$$K_{\text{th}} = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b} = K_{\text{eq}}$$

The equilibrium constant in terms of concentration is designated as K_{eq}

$$K_{\text{th}} = K_{\text{eq}} \frac{\gamma_{\text{C}}^c \gamma_{\text{D}}^d}{\gamma_{\text{A}}^a \gamma_{\text{B}}^b} (1 \text{ mol dm}^{-3})^{a+b-c-d}$$

- Q-26 For the reaction



the equilibrium concentration of each component is as follows:

$$\text{A} = 2.0 \text{ mol dm}^{-3}$$

$$\text{B} = 4.0 \text{ mol dm}^{-3}$$

$$\text{C} = 8.0 \text{ mol dm}^{-3}$$

$$\text{D} = 7.0 \text{ mol dm}^{-3}$$

What is K_{eq} for the reaction? Assuming that all the activity coefficients are unity, calculate the standard free energy value for this reaction at 298 K.

$$\begin{aligned} \text{A-26 } K &= \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]} = \frac{(8.0)(7.0)}{(4.0)(2.0)} \\ &= 7.0 \end{aligned}$$

$$K_{\text{eq}} = K_{\text{th}}$$

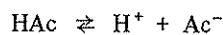
$$\Delta G^\circ = -(2.3) RT \log K_{\text{th}}$$

$$\Delta G^\circ = -(2.3) (8.31 \text{ J K}^{-1}) (298 \text{ K}) \log 7.0$$

$$\Delta G^\circ = \frac{-(2.3) (8.31 \text{ J}) (298) (0.845) (1 \text{ kJ})}{1000 \text{ J}}$$

$$\Delta G^\circ = -4.81 \text{ kJ}$$

- Q-27 For the reaction



give the expressions for K_{eq} and K_{th} . Assume that all activity coefficients are unity. What are the units for K_{eq} and K_{th} ?

(see A-25)

$$\text{A-27 } K_{\text{eq}} = \frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]}$$

K_{eq} has the units of mol dm^{-3}

$$K_{\text{th}} = K_{\text{eq}} (1 \text{ mol dm}^{-3})^{-1}$$

Notice that K_{th} is dimensionless.

- Q-28 From the relationship given between activity and partial pressure in Q-2, express the thermodynamic equilibrium constant from A-15 in terms of partial pressures.

A-28 $a = \gamma \frac{P}{P^\circ} \quad (\text{Q-2})$

$$K_{th} = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

$$a_C^c = \gamma_C^c \frac{P_C^c}{P^\circ_C}$$

$$a_D^d = \gamma_D^d \frac{P_D^d}{P^\circ_D}$$

$$a_A^a = \gamma_A^a \frac{P_A^a}{P^\circ_A}$$

$$a_B^b = \gamma_B^b \frac{P_B^b}{P^\circ_B}$$

$$K_{th} = \frac{\gamma_C^c \gamma_D^d \frac{P_C^c}{P^\circ_C} \frac{P_D^d}{P^\circ_D} \frac{P_A^a}{P^\circ_A} \frac{P_B^b}{P^\circ_B}}{\gamma_A^a \gamma_B^b \frac{P_A^a}{P^\circ_A} \frac{P_B^b}{P^\circ_B}}$$

Q-29 Assuming that all the activity coefficients in A-28 are equal to unity (ideal gases) and the standard states are 101.3 kN m^{-2} give the expression for K_{th} .

A-29 When $\gamma = 1$ and the standard states are all 101.3 kN m^{-2} , then

$$K_{th} = \frac{P_C^c P_D^d}{P_A^a P_B^b} \frac{(101.3 \text{ kN m}^{-2})^a (101.3 \text{ kN m}^{-2})^b}{(101.3 \text{ kN m}^{-2})^c (101.3 \text{ kN m}^{-2})^d} = K_p$$

The equilibrium constant in terms of partial pressures is designated as K_p .

$$K_{th} = K_p \frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} (101.3 \text{ kN m}^{-2})^{a+b-c-d}$$

Q-30 Assuming that the gases are ideal, express K_{th} and K_p for the reaction



in terms of partial pressures.

A-30 $\gamma_{\text{N}_2\text{O}_4} = \gamma_{\text{NO}_2} = 1$ (ideal gases)

$$K_p = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2}$$

$$K_{th} = K_p (101.3 \text{ kN m}^{-2})^{2-1}$$

Q-31 All K_{th} values are dimensionless. What must be the dimensions of K_p ?

A-31 $K_{th} = K_p (101.3 \text{ kN m}^{-2})$

K_p must have the dimensions of $(\text{kN m}^{-2})^{-1}$.

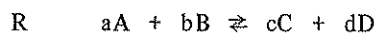
A-32 $K_{th} = 6.9$

$$K_p = \frac{K_{th}}{101.3 \text{ kN m}^{-2}}$$

$$K_p = 6.8 \times 10^{-2} \text{ m}^2 \text{ kN}^{-1}$$

Q-32 Calculate the value of K_p for the reaction given in Q-30.

$$K_{th} = 6.9$$



$$\Delta G = \Delta G^\circ + RT 2.3 \log \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

At equilibrium $\Delta G = 0$

$$\Delta G^\circ = -RT 2.3 \log K_{th}$$

$$K_{th} = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

For solutions when standard states are 1 mol dm^{-3}

$$K_{th} = K_{eq} (1 \text{ mol dm}^{-3})^{a+b-c-d} \left(\frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \right)$$

For gases when standard states are all 101.3 kN m^{-2}

$$K_{th} = K_p (101.3 \text{ kN m}^{-2})^{a+b-c-d} \left(\frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b} \right)$$

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

$$a = \gamma \frac{P}{P^\circ}$$

$$a = \gamma \frac{[C]}{[C^\circ]}$$

γ is the activity coefficient and is equal to unity for ideal gases, ideal solutions, pure solids and pure liquids.

S-2 Because of the relationship between equilibrium and standard free energy change

$$\Delta G^\circ = -RT 2.3 \log K_{th}$$

and the relationship of standard free energy change to standard enthalpy change and standard entropy change

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

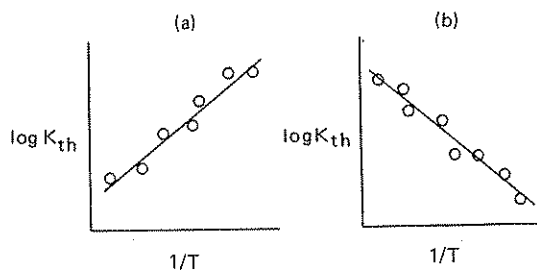
measurement of the equilibrium constant at various temperatures can be used to evaluate ΔH° and ΔS° for a chemical reaction.

A-33 $\Delta G^\circ = -RT (2.3) \log K_{th}$
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
 Set ΔG° 's equal to each other.
 $-RT (2.3) \log K_{th} = \Delta H^\circ - T\Delta S^\circ$
 Rearrange to give

$$\log K_{th} = -\frac{\Delta H^\circ}{RT (2.3)} + \frac{\Delta S^\circ}{R (2.3)}$$

Q-33 Derive a relationship between equilibrium constant and standard enthalpy and entropy changes.

Q-34 By determining the equilibrium constant at various temperatures and plotting in a graph, ΔH° and ΔS° may be found. Plots of $\log K_{th}$ vs. $\frac{1}{T}$ are given.



What is the slope equal to in the graph of $\log K_{th}$ vs. $\frac{1}{T}$?

A-34 From the equation of a straight line
 $y = ax + b$
 a is the slope.
 This can be compared with the equation

$$\log K_{th} = -\frac{\Delta H^\circ}{RT (2.3)} + \frac{\Delta S^\circ}{R (2.3)}$$

 Slope is equal to $\frac{-\Delta H^\circ}{R (2.3)}$
 Therefore, ΔH° can be found from the slope.

Q-35 What is the y intercept equal to in the graph of $\log K_{th}$ vs. $\frac{1}{T}$?

A-35 y intercept is equal to $\frac{\Delta S^\circ}{R (2.3)}$
 This is the usual way for determining the thermodynamic functions experimentally.

Q-36 What determines whether the graph in Q-34 is drawn as (a) or (b)?

- A-36 (a) if ΔH° is negative
(b) if ΔH° is positive

- Q-37 If two values of $\log K_{th}$ are known at two different temperatures

$$\log K_{th}(1) \text{ at } \frac{1}{T_1}$$

$$\log K_{th}(2) \text{ at } \frac{1}{T_2}$$

derive an expression for determining ΔH° from this information.

$$\text{slope} = \frac{(y_2 - y_1)}{(x_2 - x_1)}$$

A-37

$$\text{slope} = \frac{\log K_{th}(2) - \log K_{th}(1)}{\frac{1}{T_2} - \frac{1}{T_1}}$$

$$\text{slope} = \frac{-\Delta H^\circ}{R(2.3)}$$

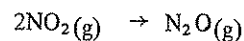
Set equal.

$$\frac{\log \frac{K_{th}(2)}{K_{th}(1)}}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{-\Delta H^\circ}{R(2.3)}$$

Rearrange to give

$$\log \frac{K_{th}(2)}{K_{th}(1)} = \frac{-\Delta H}{R(2.3)} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

- Q-38 At 298 K the thermodynamic equilibrium constant and ΔH° for the reaction



are 6.9 and -58.2 kJ respectively. What is the value of the equilibrium constant at 273 K?

Use equation derived in A-37.

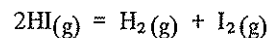
A-38

$$\log \frac{K_{th}(2)}{K_{th}(1)} = \frac{-\Delta H^\circ}{R(2.3)} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log \frac{K_{th}(2)}{8.8} = \frac{-(-58200)}{(8.31)(2.3)} \left(\frac{1}{273} - \frac{1}{298} \right)$$

$$K_{th}(2) = 59$$

- Q-39 The equilibrium constant, K_{th} , for the reaction



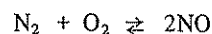
is 2.18×10^{-2} at 764 K, and is 1.64×10^{-2} at 667 K. Find ΔH° for the reaction.

A-39 $\log \frac{K_{th}(2)}{K_{th}(1)} = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

$$\log \frac{2.18 \times 10^{-2}}{1.64 \times 10^{-2}} = \frac{-\Delta H^\circ}{(8.31)(2.3)} \left(\frac{1}{764} - \frac{1}{667} \right)$$

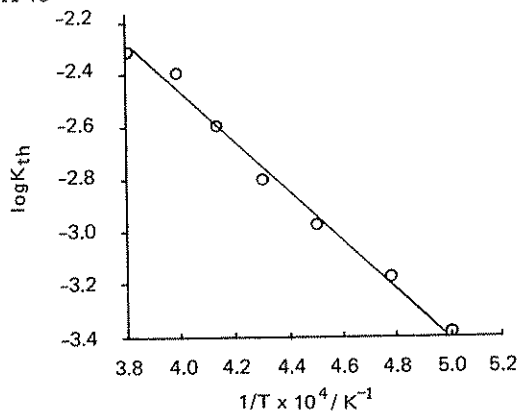
$$\Delta H = 12.5 \text{ kJ}$$

Q-40 Prepare a plot of the following experimental data for the reaction



$\log K_{th}$	$\frac{1}{T}/\text{K}^{-1}$
-2.3	3.80×10^{-4}
-2.4	4.00×10^{-4}
-2.6	4.15×10^{-4}
-2.8	4.30×10^{-4}
-3.0	4.55×10^{-4}
-3.2	4.80×10^{-4}
-3.4	5.00×10^{-4}

A-40



Q-41 Find ΔH° for the reaction by using a graphical procedure.

A-41 $\text{slope} = \frac{-\Delta H^\circ}{R(2.3)}$

$$-0.94 \times 10^4 = \frac{-\Delta H^\circ}{(8.31)(2.3)}$$

$$\Delta H^\circ = 180 \text{ kJ}$$

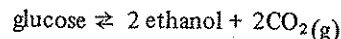
R a) $2.3 \log K_{th} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$

b) $2.3 \log \frac{K_{th}(2)}{K_{th}(1)} = \frac{-\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

S-3

Thermodynamics plays an important role in the study of biochemical reactions. The thermodynamic relationships presented in the previous sections are applied in exactly the same way to biochemical reactions as they are to chemical systems.

Q-42 The net reaction for the alcoholic fermentation of glucose is



Calculate ΔG° for this reaction from the information given below. Is this a spontaneous process under these conditions?

$$\Delta G_f^\circ (\text{glucose}) = -917 \text{ kJ mol}^{-1}$$

$$\Delta G_f^\circ (\text{ethanol}) = -181 \text{ kJ mol}^{-1}$$

$$\Delta G_f^\circ (\text{CO}_2) = -394 \text{ kJ mol}^{-1}$$

A-42
$$\Delta G^\circ = \sum n \Delta G_f^\circ (\text{product}) - \sum n \Delta G_f^\circ (\text{reactants})$$

$$\Delta G^\circ = [(2 \text{ mol}) (-394 \text{ kJ mol}^{-1}) + (2 \text{ mol}) (-181 \text{ kJ mol}^{-1})] - (1 \text{ mol}) (-917 \text{ kJ mol}^{-1})$$

$$= -788 - 362 + 917$$

$$\Delta G^\circ = -233 \text{ kJ}$$

It is spontaneous.

Q-43 Consider the following change taking place in a protein.

native state \rightleftharpoons denatured state

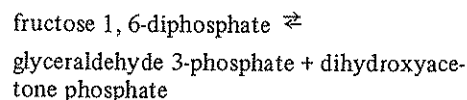
In this reaction hydrogen bonds are being broken. Consequently, the reaction is endothermic ($\Delta H^\circ = +$). If, at 40°C , the reaction is spontaneous ($\Delta G = -$), what must be the sign and magnitude of ΔS ?

What does this mean in terms of the structure of the protein?

A-43
$$\Delta G = \Delta H - T\Delta S$$

In order for the reaction to be spontaneous, ΔS° must be positive and the order of magnitude of $T\Delta S$ must be larger than ΔH . The order of the protein in the native state (helix structure) is greater than the denatured state (random structure).

Q-44 During glycolysis, fructose 1, 6-diphosphate is broken down to yield glyceraldehyde 3-phosphate plus dihydroxyacetone phosphate. During gluconeogenesis, fructose 1, 6-diphosphate is synthesized from the triose phosphates. A single enzyme, aldolase, catalyzes both these processes. The reversible reaction is



The thermodynamic equilibrium constant for this reaction going in the direction written equals 8.91×10^{-5} at 25°C . Calculate the value of ΔG° for the cleavage of fructose diphosphate.

A-44 $\Delta G^\circ = -RT \, 2.3 \log K_{th}$

$$K_{th} = 8.91 \times 10^{-5}$$

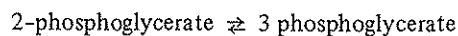
$$R = 8.31 \text{ J K}^{-1}$$

$$T = 298 \text{ K}$$

$$\Delta G^\circ = -(8.31 \text{ J K}^{-1})(298 \text{ K}) 2.3 \log 8.91 \times 10^{-5}$$

$$\Delta G^\circ = +23.1 \text{ kJ}$$

Q-45 The enzyme, phosphoglycerate mutase, catalyzes the following reaction



If at 25 °C $K_{th} = 5.80$ and at 37 °C

$K_{th} = 5.45$, calculate the values for ΔG° , ΔH° , and ΔS° for this reaction at 37 °C.

A-45 $T_2 = 273 + 37 = 310 \text{ K}$

$$T_1 = 273 + 25 = 298 \text{ K}$$

$$\log \frac{K_{th}(2)}{K_{th}(1)} = \frac{-\Delta H^\circ}{R(2.3)} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta H^\circ = \frac{-(\log \frac{5.45}{5.80})(8.31 \text{ J K}^{-1})(2.3)}{\left(\frac{1}{310 \text{ K}} - \frac{1}{298 \text{ K}} \right)}$$

$$\Delta H^\circ = 4.0 \text{ kJ}$$

$$\Delta G^\circ = -RT \, 2.3 \log K_{th}$$

$$\Delta G^\circ = -(8.31 \text{ J K}^{-1})(310 \text{ K}) 2.3 \log 5.45$$

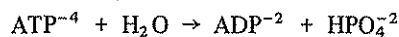
$$\Delta G^\circ = -4.4 \text{ kJ}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-4.4 = 4.0 - (310) \Delta S^\circ$$

$$\Delta S^\circ = \frac{4000 + 4400}{310} = 27 \text{ J K}^{-1}$$

Q-46 For the hydrolysis of adenosine triphosphate (ATP) to adenosine diphosphate (ADP) under standard conditions, which may be represented by

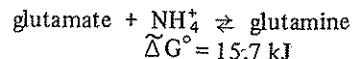


$$\Delta G^\circ = -29.3 \text{ kJ mol}^{-1}$$

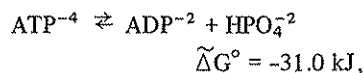
What will be the ΔG for the reaction if the concentration of ATP^{-4} , ADP^{-2} , and HPO_4^{-2} are all at concentrations of $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ at 25 °C. Assume activity coefficients to be unity.

A-49 This reaction could be coupled to a reaction with a large negative ΔG which uses ATP^{-4} . Another possibility is to couple the reaction with one which has a large negative ΔG and produces ADP^{-2} or HPO_4^{-2} . This would greatly increase the concentration of ADP^{-2} or HPO_4^{-2} .

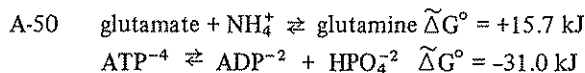
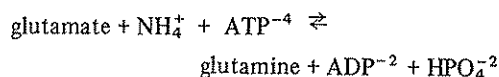
Q-50 Since most biological systems are around a pH of 7 many ΔG° values are replaced by $\tilde{\Delta G}^\circ$ values which give the standard state of H^+ as $1 \times 10^{-7} \text{ mol dm}^{-3}$. In using the $\tilde{\Delta G}^\circ$ value for calculating ΔG , no correction has to be made when using pH 7. The importance of ATP^{-4} in life processes can be shown in the coupling procedure in which a cell uses ATP^{-4} to supply the driving force in the biosynthesis of glutamine.



If this reaction is coupled with the reaction

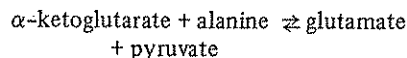


what is the $\tilde{\Delta G}^\circ$ for the overall reaction?



This net reaction does not proceed by two separable stages, but probably involves an intermediate such as glutamylphosphate-enzyme.

Q-51 Glutamate can be synthesized by transamination of its α -oxo-acid precursor (α -ketoglutarate) with L-alanine



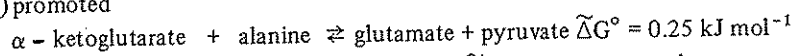
At pH 7 and 25°C , $\tilde{\Delta G}^\circ$ is 0.25 kJ mol^{-1} proceeding in the direction written.

Will the spontaneous formation of glutamate be promoted by coupling this transamination reaction with

a) a reaction in which pyruvate is oxidized to yield acetyl-Co A
 $\tilde{\Delta G}^\circ = -258 \text{ kJ mol}^{-1}$

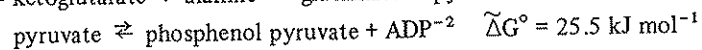
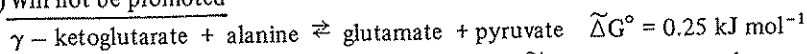
b) a reaction which yields pyruvate from phosphoenolpyruvate plus ADP^{-2}
 $\Delta G^\circ = -25.5 \text{ kJ mol}^{-1}$?

A-51 a) promoted



$$\tilde{\Delta}G^\circ \text{ coupled} = -258 \text{ kJ mol}^{-1}$$

b) Will not be promoted



$$\tilde{\Delta}G^\circ \text{ coupled} = +25.7 \text{ kJ mol}^{-1}$$

R Thermodynamics can be applied to biochemical reactions to yield important knowledge about the energetics of life processes. A reaction with a positive ΔG° may be made to take place by coupling it with a reaction which has a negative ΔG° .

$\tilde{\Delta}G^\circ$ is the standard free energy change at pH 7 under otherwise standard conditions.

TABLE I
STANDARD HEATS OF FORMATION, ΔH_f°

Compound	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	Compound	$\Delta H_f^\circ / \text{kJ mol}^{-1}$	Compound	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
Al(s)	0.00	C ₅ H ₁₂ (g)	-146	H ₂ O ₂ (l)	-188
Al ₂ O ₃ (s)	-1670	C ₅ H ₁₂ (l)	-173	I ₂ (g)	62.3
Br ₂ (g)	30.7	C ₆ H ₆ (g)	82.9	I ₂ (s)	0.00
Br ₂ (l)	0.00	C ₆ H ₆ (l)	49.0	N ₂ (g)	0.00
Ca(s)	0.00	C ₆ H ₁₂ (l)	-41.7	NH ₃ (g)	-46.2
C(g)	718	C ₆ H ₁₄ (g)	-167	N ₂ O(g)	81.6
C(graphite)	0.00	C ₆ H ₁₄ (l)	-199	NO(g)	90.4
CaCO ₃ (s)	-1207	CH ₃ OH(g)	-201	NO ₂ (g)	33.8
CaO(s)	-636	C ₂ H ₅ OH(g)	-237	N ₂ O ₄ (g)	9.66
Cl ₂ (g)	0.00	CO(g)	-111	O ₂ (g)	0.00
CH ₄ (g)	-74.8	CO ₂ (g)	-394	O ₃ (g)	142
C ₂ H ₂ (g)	227	H ₂ (g)	0.00	S(s)	0.00
C ₂ H ₄ (g)	52.3	HBr(g)	-36.2	Si(s)	0.00
C ₂ H ₆ (g)	-84.7	HCl(g)	-92.3	SiO ₂ (s)	-859
C ₃ H ₆ (g)	20.4	HI(g)	25.9	SO ₂ (g)	-297
C ₃ H ₈ (g)	-104	H ₂ O(g)	-242	SO ₃ (g)	-395
C ₄ H ₁₀ (g)	-125	H ₂ O(l)	-286		

From *Selected Values of Chemical Thermodynamic Properties*, ed. F. A. Rossini, et al., National Bureau of Standards Circular 500

TABLE II
STANDARD ENTROPIES, S°

Compound	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$	Compound	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$	Compound	$S^\circ / \text{J mol}^{-1} \text{K}^{-1}$
Al(s)	28.3	C ₅ H ₁₂ (g)	348	I ₂ (g)	261
Al ₂ O ₃ (s)	51.0	C ₅ H ₁₂ (l)	263	I ₂ (s)	117
Br ₂ (g)	245.2	C ₆ H ₆ (g)	269.2	N ₂ (g)	192
Br ₂ (l)	152	C ₆ H ₆ (l)	173	NH ₃ (g)	192
Ca(s)	41.6	C ₆ H ₁₂ (l)	386	N ₂ O(g)	220
C(g)	158	C ₆ H ₁₄ (g)	387	NO(g)	211
C(graphite)	5.73	C ₆ H ₁₄ (l)	294	NO ₂ (g)	240
CaCO ₃ (s)	92.9	CH ₃ OH(g)	238	N ₂ O ₄ (g)	304
CaO(s)	39.8	C ₂ H ₅ OH(g)	282	O ₂ (g)	205
Cl ₂ (g)	223	CO(g)	198	O ₃ (g)	238
CH ₄ (g)	186	CO ₂ (g)	214	S(s)	31.9
C ₂ H ₂ (g)	201	H ₂ (g)	131	Si(s)	18.7
C ₂ H ₄ (g)	219	HBr(g)	198	SiO ₂ (s)	41.8
C ₂ H ₆ (g)	230	HCl(g)	187	SO ₂ (g)	249
C ₃ H ₆ (g)	267	HI(g)	206	SO ₃ (g)	256
C ₃ H ₈ (g)	270	H ₂ O(g)	189		
C ₄ H ₁₀ (g)	310	H ₂ O(l)	70.0		

From *Selected Values of Chemical Thermodynamic Properties*, ed. F. A. Rossini, et al., National Bureau of Standards Circular 500.

TABLE III
STANDARD FREE ENERGY OF FORMATION, ΔG_f°

Compound	$\Delta G_f^\circ / \text{kJ mol}^{-1}$	Compound	$\Delta G_f^\circ / \text{kJ mol}^{-1}$	Compound	$\Delta G_f^\circ / \text{kJ mol}^{-1}$
Al(s)	0.00	C ₅ H ₁₂ (g)	-8.20	I ₂ (g)	19.4
Al ₂ O ₃ (s)	-1576	C ₅ H ₁₂ (l)	-9.25	I ₂ (s)	0.00
Br ₂ (g)	3.14	C ₆ H ₆ (g)	130	N ₂ (g)	0.00
Br ₂ (l)	0.00	C ₆ H ₆ (l)	124	NH ₃ (g)	-16.6
Ca(s)	0.00	C ₆ H ₁₂ (l)	87.0	N ₂ O(g)	104
C(g)	673	C ₆ H ₁₄ (g)	0.21	NO(g)	86.7
C(graphite)	0.00	C ₆ H ₁₄ (l)	87.0	NO ₂ (g)	51.8
CaCO ₃ (s)	-1129	CH ₃ OH(g)	-162	N ₂ O ₄ (g)	98.3
CaO(s)	-604	C ₂ H ₅ OH(g)	-170	O ₂ (g)	0.00
Cl ₂ (g)	0.00	CO(g)	-137	O ₃ (g)	163.0
CH ₄ (g)	-50.8	CO ₂ (g)	-394	S(s)	0.00
C ₂ H ₂ (g)	209	H ₂ (g)	0.00	Si(s)	0.00
C ₂ H ₄ (g)	68.1	HBr(g)	-53.2	SiO ₂ (s)	-805.0
C ₂ H ₆ (g)	-32.9	HCl(g)	-95.3	SO ₂ (g)	-300.2
C ₃ H ₆ (g)	62.7	HI(g)	1.30	SO ₃ (g)	-370.4
C ₃ H ₈ (g)	-23.5	H ₂ O(g)	-229		
C ₄ H ₁₀ (g)	-15.7	H ₂ O(l)	-237.2		

From *Selected Values of Chemical Thermodynamic Properties*, ed. F. A. Rossini, et al., National Bureau of Standards Circular 500.

TABLE IV
BOND ENERGIES

<u>Bond</u>	<u>Bond energy/ kJ mol⁻¹</u>	<u>Bond</u>	<u>Bond energy/ kJ mol⁻¹</u>	<u>Bond</u>	<u>Bond energy/ kJ mol⁻¹</u>
Br—Br	192	C = O	724	N — H	385
C — C	335	C ≡ O	1071	N — N	155
C = C	607	Cl — Cl	238	N ≡ N	941
C ≡ C	812	F — F	159	N = O	628
C — Cl	326	H — Br	368	O — H	456
C — F	485	H — Cl	431	O — O	138
C — H	414	H — F	565	O = O	490
C — N	293	H — H	431	S—H	356
C ≡ N	887	H — I	297		
C — O	343	I — I	151		

From *Selected Values of Chemical Thermodynamic Properties*, ed. F. A. Rossini, et al., National Bureau of Standards Circular 500.

Recommended Readings

- Klotz, Irving M. 1967. *Energy changes in biochemical reactions*. New York: Academic Press.
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