

For 2 temps, T_1 and T_2

$$\ln K_1 = -\frac{\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R} \quad \left(K_1 = K_{eq} \text{ at } T_1 \right)$$

$$\ln K_2 = -\frac{\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R} \quad \text{etc.}$$

... subtracting,

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right] = \frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\boxed{\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]} \quad \text{Van't Hoff equn.}$$

Very useful

e.g. (i) Can get ΔH° by knowing K 's at two T 's.

(ii) Can get K_2 (different temp) by knowing K_1 and ΔH°

Two situations:

(1) Rx. is exothermic, (ΔH° is -ve)
and $T_2 > T_1$

Then RHS is -ve

i.e. $\ln \frac{K_2}{K_1}$ is -ve

$\therefore K_1$ must be $> K_2$

i.e. for an exothermic rx. an increase in temp. shifts the equilib. $L \leftarrow R$ - favours reactants

(2) Rx. is endothermic (ΔH° +ve)

RHS is +ve

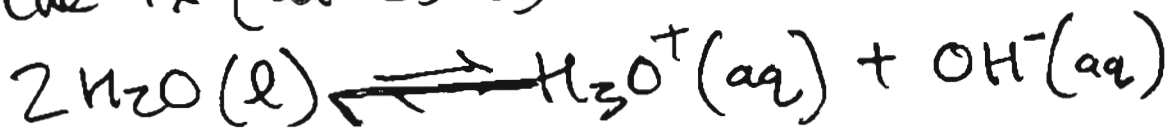
$\ln \frac{K_2}{K_1}$ is +ve

$\therefore K_2 > K_1$ - rx. goes $L \rightarrow R$ at higher T.

An increase in temp. shifts a rx. in the direction in which heat is absorbed

⑧ This is in accord with Le Chatelier.

Q For the rx (at 25°C)



$$K_w = 1.00 \times 10^{-14} \text{ and } \Delta H^\circ(298) = +55.8 \text{ kJ}$$

Calculate the pH of boiling water

Remember $K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = [\text{H}_3\text{O}^+]^2$ since

-also $\text{pH} = -\log[\text{H}_3\text{O}^+]$

$[\text{H}_3\text{O}^+] = [\text{OH}^-]$ in pure water.

∴ we need K_w at 100°C

∴ we need ΔG°_{373}

Long way

Short way
- use van't Hoff equn.

$$\Delta G^\circ_{298} = -RT \ln K = -298 \times 8.314 \ln 1 \times 10^{-14}$$
$$= \underline{8.0 \times 10^4 \text{ J mol}^{-1}}$$

$$\Delta G^\circ_{298} = 8 \times 10^4 \text{ J} = \Delta H^\circ - T\Delta S^\circ \leftarrow \text{GET}$$

$$\Delta S^\circ = \underline{-81 \text{ J K}^{-1} \text{ mol}^{-1}}$$

↑ substitute 55.8 ↑ 298

OK, so $\Delta G^\circ_{373} = \Delta H^\circ - T\Delta S^\circ = 55.8 \times 10^3 - [373(-81)]$

$$\Delta G^\circ_{373} = 86 \times 10^3 \text{ J}; K_{373} = e^{-\frac{\Delta G^\circ}{RT}} = e^{-\frac{86 \times 10^3}{(8.314)(373)}}$$

$$K = 9 \times 10^{-13} = [\text{H}_3\text{O}^+]^2$$

$$\text{pH} = \underline{6.02} \text{ at } 100^\circ\text{C}$$

(87)

BIOENERGETICS and coupled rxs

Example metabolism of glucose / Glycolysis: converting glucose \rightarrow pyruvate

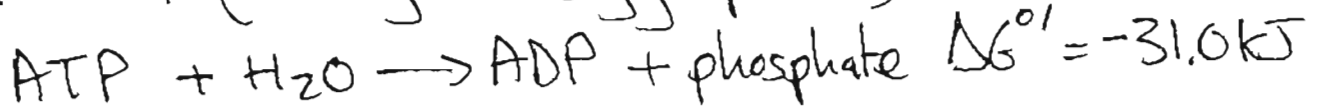
The first step is the formation of glucose-6-phosphate. But.. the direct rx. is endergonic



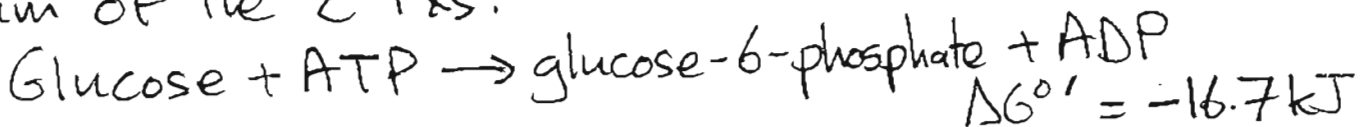
$$\Delta G^{\circ'} = 14.3 \text{ kJ}$$

Does not go forward!!

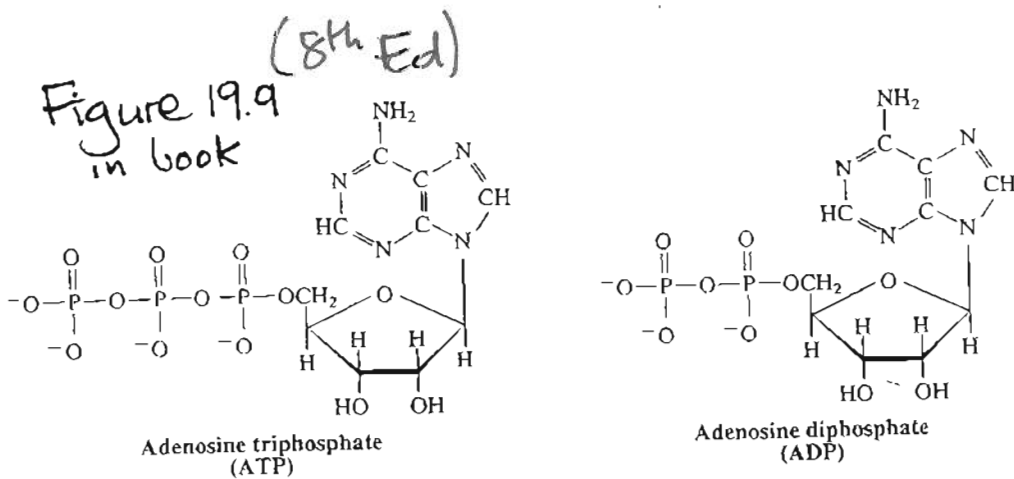
So, this reaction is coupled to the hydrolysis of ATP (a high energy species)



Sum of the 2 rxs:



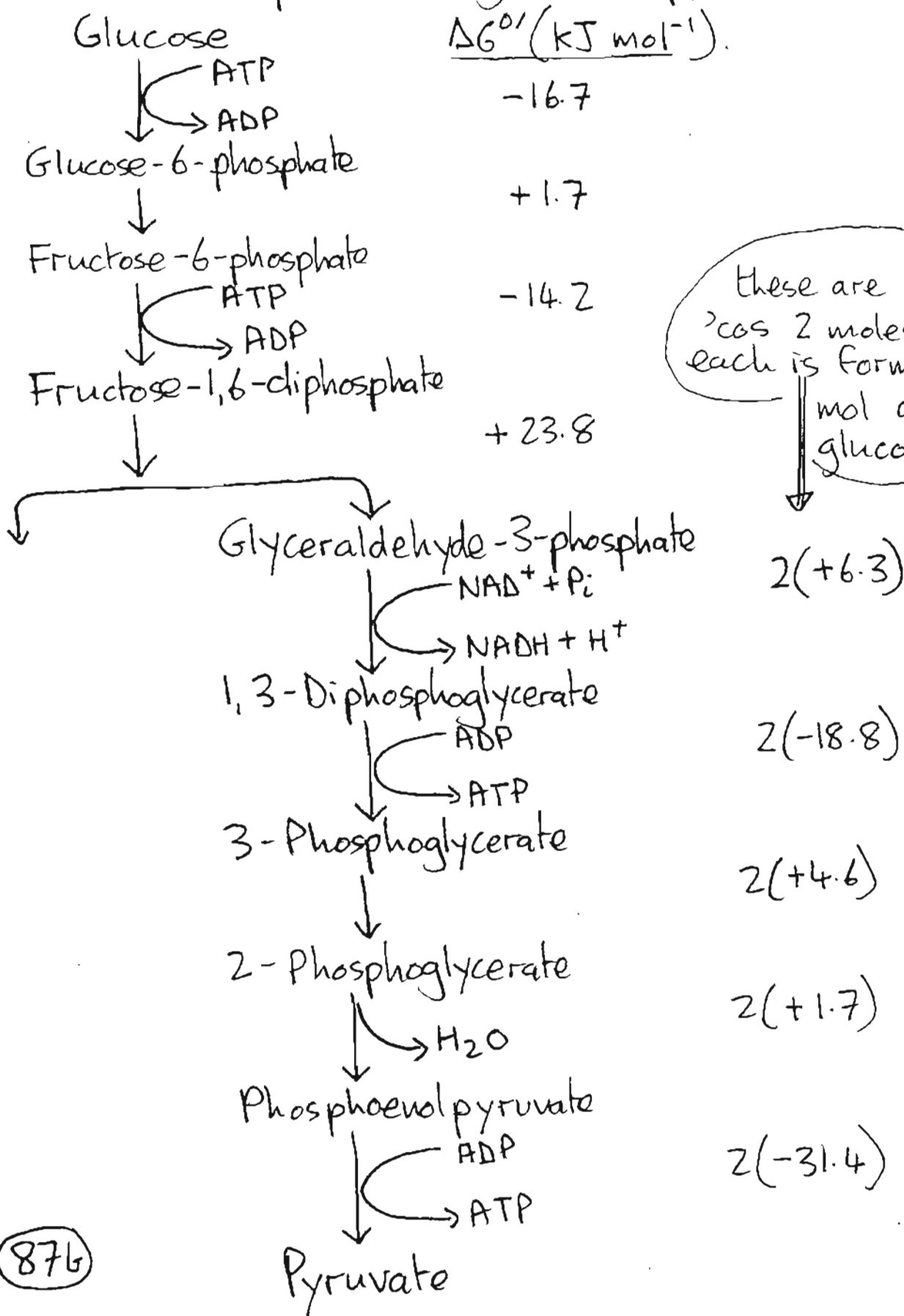
exergonic ... good!!



87a

Fig. 18.9 (9th ed.) is messy (balls & sticks)

The overall process in glucose \rightarrow pyruvate is:

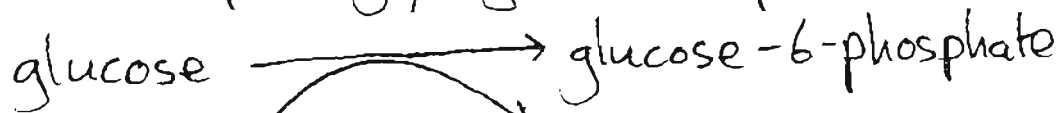


these are $\times 2$
 'cos 2 moles of each is formed per mol of glucose

(876)

Notes:

A. The first step of glycolysis is represented as,

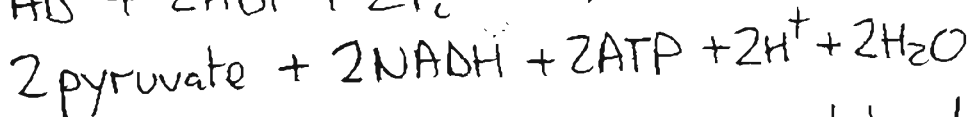
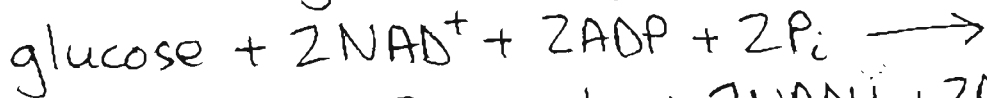


ATP

ADP

The two rxns are coupled

The overall glucose \rightarrow pyruvate rx is:



$\Delta G^{\circ'} = -80 \text{ kJ}$; all the steps are enzyme catalysed.

B. NAD^+ is nicotinamide adenine dinucleotide

NADH is the reduced form

P_i is the available inorganic phosphates, e.g. PO_4^{3-} , HPO_4^{2-} , H_2PO_4^-

C. The given ΔG values are denoted $\Delta G^{\circ'}$.

This refers to the biological std. state; i.e. under physiological conditions, pH 7 (so $[\text{H}^+] = 1 \times 10^{-7} \text{ mol L}^{-1}$)

What this means is that although the std. state quantities ~~ΔG°~~ ΔG° and $\Delta G^{\circ'}$ are different, the overall ΔG_{rx} remains unchanged, regardless of the std. state used.

D. There are other phosphates having large, negative $\Delta G^{\circ'}$ values. These also can be used for carrying out work (i.e. driving non-spontaneous endergonic rxns.)

(87c) e.g. acetyl phosphate $-43.1 \text{ kJ mol}^{-1}$ } $\Delta G^{\circ'}$ values
pyrophosphate $-33.5 \text{ kJ mol}^{-1}$ }

What can we do with tables of ΔH_f° , ΔG_f° and $S^\circ(298K)$?

1. $\Delta G_{rx}^\circ(298) = \underbrace{\sum \Delta G_f^\circ(\text{prods}) - \sum \Delta G_f^\circ(\text{reacts})}_{K_{eq}(298)} \quad K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}$

2. $\Delta H_{rx}^\circ(298) = \sum \Delta H_f^\circ(\text{prods}) - \sum \Delta H_f^\circ(\text{reacts})$

$$\Delta S_{rx}^\circ(298) = \sum S^\circ(\text{prods}) - \sum S^\circ(\text{reacts})$$

$\Delta G_{rx}^\circ = \Delta H_{rx}^\circ - T\Delta S_{rx}^\circ$
(assumes $\Delta H^\circ, \Delta S^\circ$ indep. of T)

$\Delta G_{rx}^\circ(\text{temp } T) \xrightarrow{K_{eq} = e^{-\frac{\Delta G^\circ}{RT}}} K_{eq}(\text{temp } T)$

3. Calc. T at which $K_{eq} = 1$ (e.g. m.p., b.p.)

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0 \quad ; \quad \boxed{T = \frac{\Delta H^\circ}{\Delta S^\circ}}$$

4. At what T will K_{eq} have some particular value?
(not 1)

(a) $\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$ solve for T .

(b) $\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$

Get ΔH° from $\sum \Delta H_f^\circ(\text{prods}) - \sum \Delta H_f^\circ(\text{reacts})$.

K_1, K_2, T_1 known ... get T_2

Summary since last (page 54) summary.

- Entropy $\Delta S = \frac{q_{rev}}{T}$ (equib. process); $\Delta S > \frac{q}{T}$
 - determines direction of spont. change (spont rx)
 - need to maximise entropy (disorder)
- 2nd Law $\rightarrow \Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} > 0$; Rx \rightarrow
 $\Delta S_{univ} < 0$; Rx \leftarrow
 $\Delta S_{univ} = 0$; Rx @ equilibrium
- 3rd Law - at absolute 0, $S = 0$
 - hence entropy inc. with T
 - std. molar entropy S° ($\Delta S^\circ_{rx} = \sum S^\circ_{prods} - \sum S^\circ_{reacts}$)
 - factors affecting S
 - entropy & phase changes; $\frac{\Delta H_{fus}}{T}$ (or ΔH_{vap}) (equilibrium)

• Gibbs Free Energy

- to get around calc. out ΔS_{surr} , we combine ΔH_{sys} & ΔS_{sys}
 $\Rightarrow \Delta G = \Delta H - T\Delta S$ (note, ΔG is T dependent)

ΔG -ve, L \rightarrow R; ΔG +ve, L \leftarrow R; $\Delta G = 0$, equilib.
↑ sign, magnitude imp.

Std. molar free energy of formation, ΔG_f°

$$\Delta G^\circ_{rx} = \sum \Delta G_f^\circ(\text{prods}) - \sum \Delta G_f^\circ(\text{reacts})$$

Concn. & free energy

$$\Delta G_{rx} = \Delta G^\circ_{rx} + RT \ln Q$$

ΔG°_{rx} and K

At equilib., $Q = K$ and $\Delta G_{rx} = 0$; $\Delta G^\circ_{rx} = -RT \ln K$

ΔG_{rx} and Q

$$\Delta G_{rx} = -RT \ln K + RT \ln Q = RT \ln \frac{Q}{K}$$

Temp. and the equilib. const.

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad \text{or} \quad \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_2 T_1} \right)$$

↑
can plot

Agrees with Le Chatelier.

- Bioenergetics ... coupled rxns \rightarrow exergonic rxns.

SUMMARY of EQUATIONS

$$\Delta U = q + w \quad ; \quad w = -P\Delta V$$

$$\Delta H = \Delta U + P\Delta V; = \Delta U + \Delta nRT; = \Delta U + nR\Delta T$$

$$c = \frac{q}{\Delta T} \quad ; \quad q = c\Delta T; \quad \begin{array}{l} q_v = \Delta U, \quad q_p = \Delta H \\ \text{Const. P, } \Delta H = C_p\Delta T \\ \text{Const. V, } \Delta U = C_v\Delta T \end{array}$$

$$q_{rx} = -q_{surr}$$

↑ various

$$\Delta H_{rx}^{\circ} = \sum \Delta H_f^{\circ}(\text{prods}) - \sum \Delta H_f^{\circ}(\text{reacts})$$

$$E = \frac{kQ_1Q_2}{r} \quad \text{ionic compds}$$

$$\Delta S > \frac{q}{T} \quad (\text{spont.})$$

$$\Delta S = \frac{q_{rev}}{T} \quad ; \quad T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}} \quad ; \quad \Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} > 0$$

$$\Delta S_{rx}^{\circ} = \sum S^{\circ}(\text{prods}) - \sum S^{\circ}(\text{reacts})$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = -T\Delta S_{total}$$

$$\Delta G_{rx}^{\circ} = \sum \Delta G_f^{\circ}(\text{prods}) - \sum \Delta G_f^{\circ}(\text{reacts}) @ 298K.$$

$$\Delta G_{rx} = \Delta G_{rx}^{\circ} + RT \ln Q$$

$$\Delta G_{rx}^{\circ} = -RT \ln K; \quad \Delta G_{rx} = RT \ln Q/K$$

$$\ln K = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}; \quad \ln \frac{K_2}{K_1} = \frac{\Delta H^{\circ}}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

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