- HW //
- Example 3-2, page 57
- Example 3-3, page 59
- Example 3-4, page 59

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Heat content (enthalpy):

- Enthalpy is the heat content of a system, or the amount of energy within a substance, both kinetic and potential.
- The increase in enthalpy, ΔH, is equal to the heat absorbed by the system at constant pressure.
- It is also the heat required to increase the internal energy and to perform the work of expansion,

$$Q_p = H_2 - H_1 = \Delta H$$

- The first law equation become:

$$\Delta H = \Delta E + P\,\Delta V$$

Table: Modified First-Law Equations for Processes Occurring Under Various Conditions

Specific condition		Process	Common means for establishing the condition	Modification for the first law dE=dq + dw under the stated condition
Constant heat	$dq = 0$	Adiabatic	Insulated vessel	dE = dw
Reversible process at constant temperature	$dT = 0$	isothermal	Constant temp bath	$dW = W_{max}$
Constant volume	$dV = 0$	Isometric (isochoric)	Closed vessel of constant volume	dW=-pdV=0 dE=Qv
Constant pressure	$dP = 0$	isobaric	Reaction occurring in an open container at constant atmospheric pressure	dH = Qp dE=dH-Pdv

Thermochemistry

- It is the study that deals with the heat changes accompanying isothermal chemical reactions at constant pressure or volume, from which values of ΔH or ΔE can be obtained.

Heat of Formation

- For any reaction represented by the chemical equation

$$aA + bB \rightarrow cC + dD$$

- the enthalpy change can be written as

$$\Delta H = \sum \overline{H}_{\text{products}} - \sum \overline{H}_{\text{reactants}}$$

$$\Delta H = c\overline{H}_{\text{C}} + d\overline{H}_{\text{D}} - a\overline{H}_{\text{A}} - b\overline{H}_{\text{B}}$$

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Entropy (S) and Disorder

- Entropy can be defined as the measure of randomness or disorder in the universe.
- Is a quantitative measure of increasing the probability of spontaneous process. From statistical mechanics we had seen that ΔS increases during a spontaneous process, so these results give us :

  $\Delta S < 0$ for non spontaneous processes
  $\Delta S = 0$ for a system at equilibrium
  $\Delta S > 0$ for spontaneous processes

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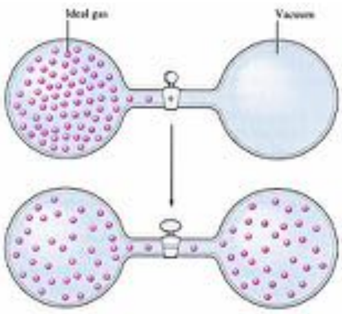
Entropy, S: what is it?

= ***the dispersal of** matter **and energy***



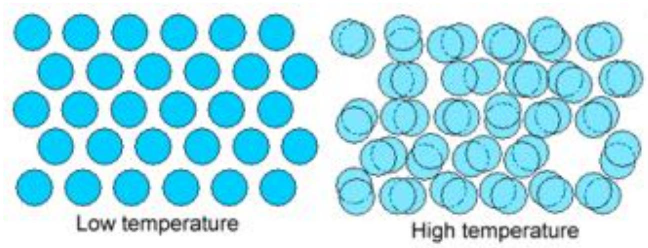
Δ Enthalpy determines **Δ Entropy**
thermodynamic favourability of transformation
(spontaneous conversion of heat to work and reverse) = (2^{nd} law of thermodynamic)

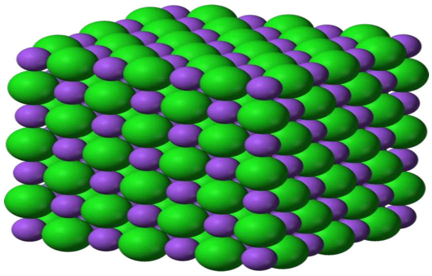
Second law of thermodynamic

- Spontaneous processes always proceeds in the direction of increased the entropy; when the system finally reaches the equilibrium, the net entropy change undergone by the system and its surrounding is equal to zero.
- The isothermal expansion of an ideal gas increases the entropy because of the enhanced number of configurations in a larger volume compared to a smaller one (more disordered)

The Third law of thermodynamics

At absolute zero , all the modes of motion stops: no vibration, no rotation and no translation), thus
The entropy of a perfect crystal, at absolute zero kelvin, is exactly equal to zero.





ΔG, Gibbs Free Energy

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

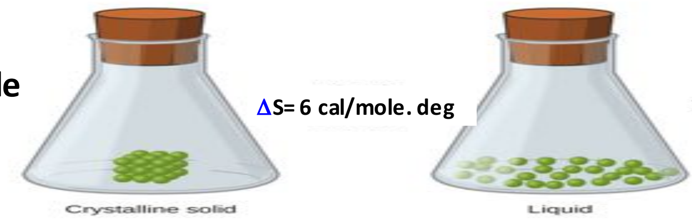
ΔG, indicates whether transformation is *thermodynamically favourable*

Thermodynamic favorability = **direction which results in:**
ΔG = -ve
(at constant T and P)

Case study

- Conversion of ice into water at 25ºC requires an absorption of heat of **1650 cal/mole**, the reaction leads to a more probable arrangement of the molecules; that is, an increased freedom of molecular movement. Hence, the entropy increases, and Δ*S* = **6 cal/mole deg** is sufficiently positive to make Δ*G* **negative**, despite the positive value of ΔH.

ΔG= -138 cal/mole



25ºC,
ΔH= 1650 cal/mole

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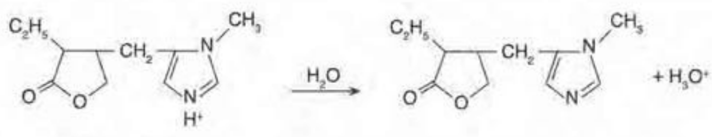

Fig. 3–7. Reaction of pilocarpinium ion to yield pilocarpine base.

calculate ΔG° at 25°C. What is the significance of the signs and the magnitudes of ΔH°, ΔS°, and ΔG°?

Answers:

$$\Delta H^\circ = 9784 \text{ cal/mole}$$
$$= 40.94 \text{ kJ/mole}$$
$$\Delta S^\circ = 1.30 \text{ cal/mole deg}$$
$$\Delta G^\circ_{25^\circ} = \Delta H^\circ - T\Delta S^\circ = 9397 \text{ cal/mole}$$

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Poly-protic ionization process

$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$; $\Delta H^\circ = -3.1$ kcal/mole **K_1= 7.5 x 10 $^{-3}$**

$H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$; $\Delta H^\circ = 0.9$ kcal/mole **K_2= 6.2 x 10 $^{-8}$**

$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$; $\Delta H^\circ = 4.5$ kcal/mole **K_3= 2.1 x 10 $^{-13}$**

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Pharmaceutical applications of ΔG

- Solubility
- Ionization
- Diffusion and permeation
- Complexation
- Chemical potential
- Stability of pharmaceutical preparations
- Mixing and separation of multi-phase system
- Understanding acid base reactions

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Summary

- The quantitative relationships among different forms of energy were reviewed and expressed in the three laws of thermodynamics.
- Gibbs free energy and spontaneity of processes were reviewed.
- Different applications of thermodynamic to pharmacy were discussed.

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Thanks for your attention

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