



Chapter (3)

Application of the 2nd and 3rd laws of thermodynamics on chemical change:

Gibbs Free Energy of Reactions

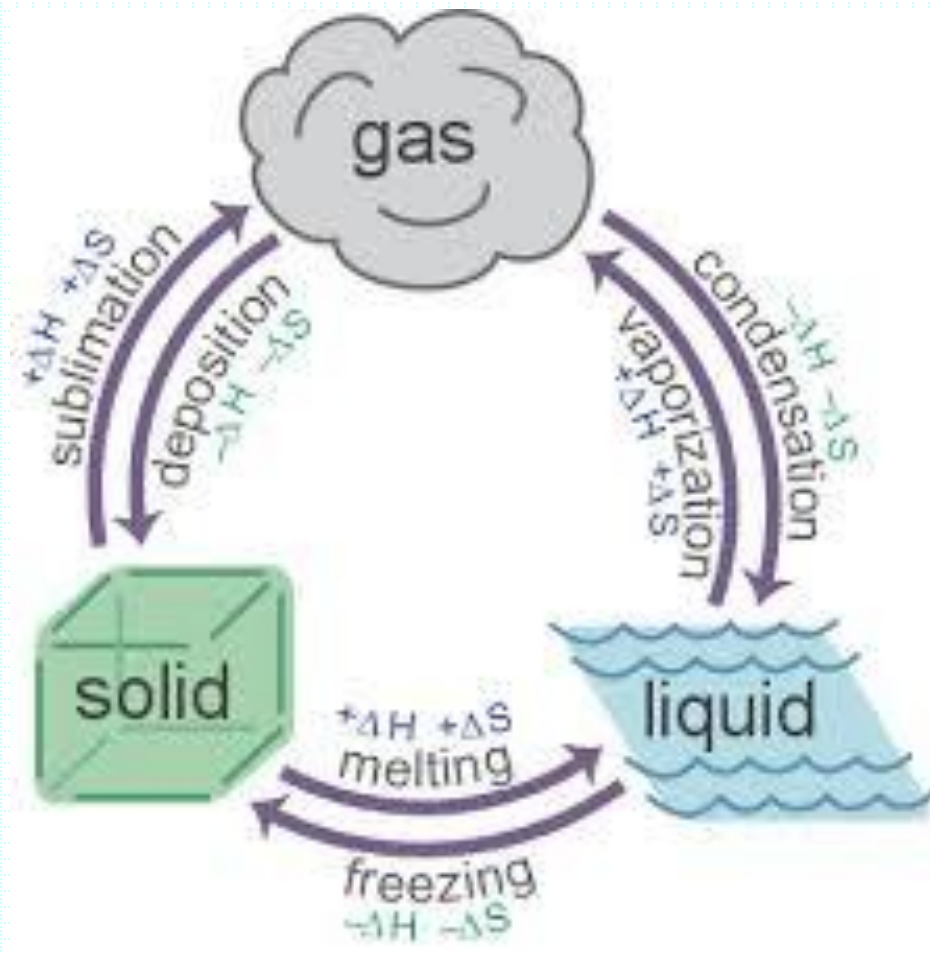
Entropy Change of phase transition

- Entropy of fusion

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T_f}$$

- Entropy of vaporization

$$\Delta_{vap}S = \frac{\Delta_{vap}H}{T_b}$$



Entropy Change of phase transition

- To evaluate entropies of transition at Temperatures other *than the* transition temperature:

Q. Entropy change of vaporization of water at 25°C?

Sum of:

- ΔS for heating from 25°C to 100°C
- ΔS for vaporization at 100°C, and
- ΔS for cooling vapor from 100°C to 25°C.

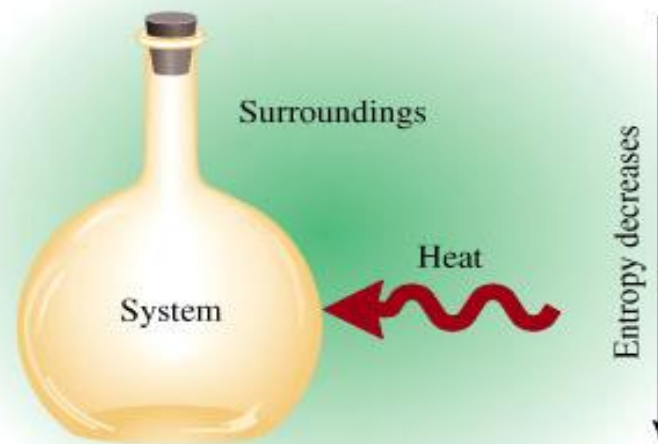
(ANS: +118 J/K.mol).

Entropy Changes in the Surroundings (ΔS_{surr})



Exothermic Process

$$\Delta S_{\text{surr}} > 0$$



Endothermic Process

$$\Delta S_{\text{surr}} < 0$$

Entropy Changes in the Surroundings (ΔS_{surr})

Entropy Changes in Surroundings

1. Heat that flows into or out of the system also changes the entropy of the surroundings*.
2. For **an isothermal process**:

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T}$$

3. At **constant pressure**, q_{sys} is simply ΔH° for the system.

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{T} = \frac{-\Delta H^\circ}{T}$$

*Surrounding is taken as heat reservoir, i.e. heat transfer does not affect its temperature

Concept of Gibbs Free Energy

- Introduced by J.W. Gibbs to combine the calculations of 2 entropies, into one.
- Because $\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ and $\Delta S_{\text{surr}} = -\Delta H/T$
- At constant T and P:
$$\Delta S_{\text{tot}} = \Delta S - \Delta H/T \quad \text{OR} \quad \Delta H - T \cdot \Delta S = -T \cdot \Delta S_{\text{tot}}$$
- Introduce $G = H - TS$ (Gibbs “Free” energy)
- Then $\Delta G = \Delta H - T \cdot \Delta S$ (constant T)
- So that $\Delta G = -T \cdot \Delta S_{\text{tot}}$ (constant T and P)

Conclusion:

In a spontaneous change (ΔS_{tot} *increases*) at constant temperature and pressure, the Gibbs energy *decreases*

Gibbs Free Energy

- $T \Delta S_{\text{tot}}$ is defined as the Gibbs free energy, ΔG .
(*tot = univ*)

For spontaneous processes: $\Delta S_{\text{univ}} > 0$

And therefore: $\Delta G < 0$

ΔG is easier to determine than ΔS_{univ} .

So:

Use ΔG to decide if a process is spontaneous.

Gibbs Free Energy

Spontaneous process (irrev.):

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

Equilibrium process (reversible):

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

For a constant-temperature process or reaction:

Gibbs free energy (G)

$$\Delta G = \Delta H_{\text{sys}} - T \cdot \Delta S_{\text{sys}}$$

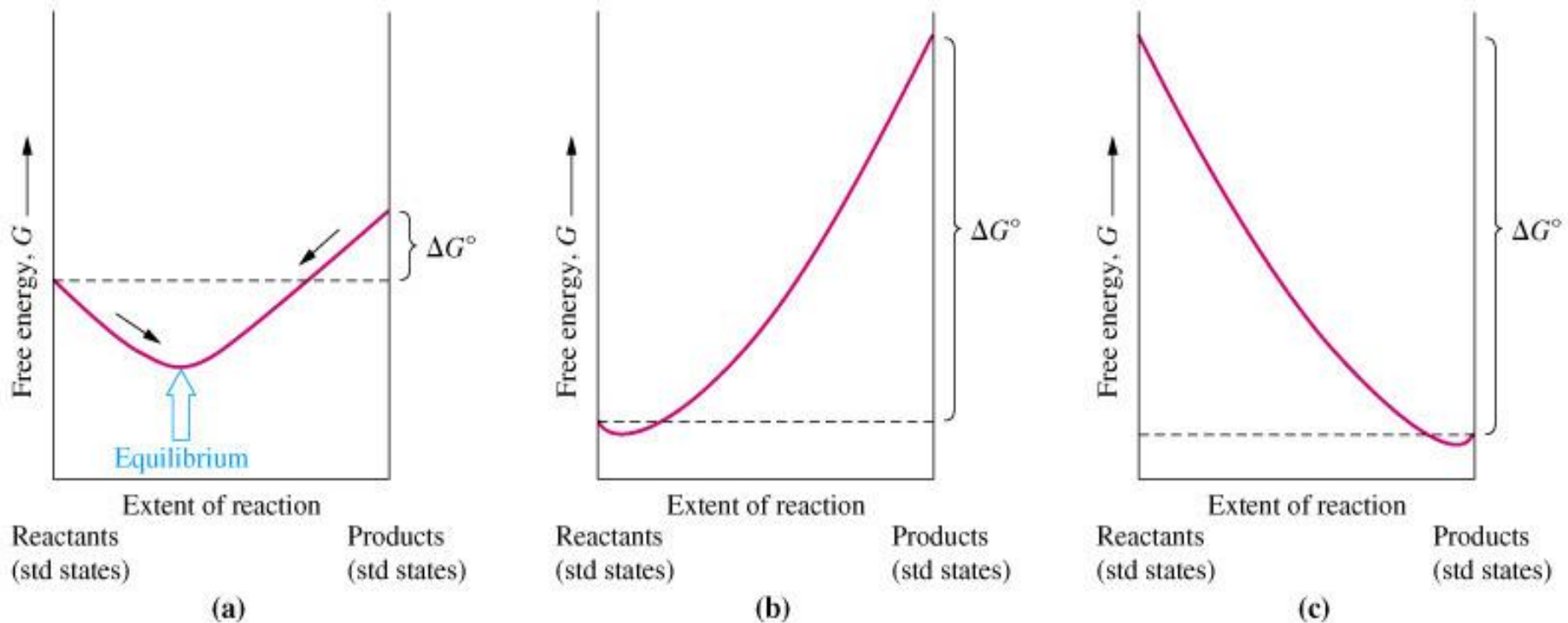
$\Delta G < 0$ The reaction is spontaneous in the forward direction.

$\Delta G > 0$ The reaction is non-spontaneous as written.
 The reaction is spontaneous in the reverse direction.

$\Delta G = 0$ The reaction is at equilibrium.

Criteria for Spontaneous Change

The direction of spontaneous change is the direction in which the free energy decreases.



Thermodynamics and Spontaneity

Spontaneous change: the direction of change that does not require work (outside assistance) to bring it about

Spontaneous chemical reactions often are exothermic:

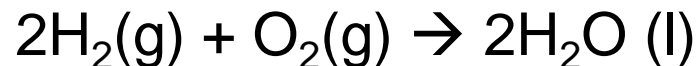
Ice melting, water vaporization, NaI dissolving in water are all spontaneous processes, yet are Endothermic.

Accompanied by an increase in the “randomness” of the distribution of the particles. An increase in ENTROPY (S)

2nd LAW: Spontaneous changes in the universe are accompanied by an increase in disorder of the universe

Spontaneity of reactions

Consider the reaction:



$$\begin{aligned}\Delta_r S^0 &= 2(70 \text{ J/K.mol}) - [2(131 \text{ J/K.mol}) - (-205 \text{ J/K.mol})] \\ &= -327 \text{ J/K.mol}\end{aligned}$$

But this reaction is spontaneous...

When considering the implications of entropy, we must always consider the total change of the system and its surroundings

$$\Delta_r H^0 = -572 \text{ kJ/mol. } T = 298 \text{ K}$$

$$\text{Therefore } \Delta_r S_{\text{sur}} = \Delta_r H^0 / T = +1920 \text{ J/K.mol}$$

$$\Delta_r S_{\text{tot}} = -327 + 1920 = +1593 \text{ J/K.mol} \quad (+\text{ve: spontaneous reaction}).$$

Substance	$S_m^0 / \text{JK}^{-1}\text{mol}^{-1}$
Gases	
Ammonia, NH_3	192.5
Carbon dioxide, CO_2	213.7
Helium, He	126.2
Hydrogen, H_2	130.7
Neon, Ne	146.3
Nitrogen, N_2	191.6
Oxygen, O_2	205.1
Water vapour, H_2O	188.8
Liquids	
Benzene, C_6H_6	173.3
Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$	160.7
Water, H_2O	69.9

Maximum non-expansion work

The fact that $\Delta G = W_{\text{net}}$
can be derived as follows:

$$dU = \delta q + \delta (W_{\text{net}} + W_{\text{expansion}})$$

$$dS = \delta q / T$$

$$T.dS = dU - (W_{\text{net}} - W_{\text{expansion}})$$

$$W_{\text{net}} = dU + P.dV - T.dS = dH - T.dS$$

For constant pressure and temperature:

$$W_{\text{net}} = dH - T.dS = dG$$

Third Law

- Entropies of all perfectly crystalline substances are the same at $T=0$.

$$\Delta S_T = S_T - S_0$$

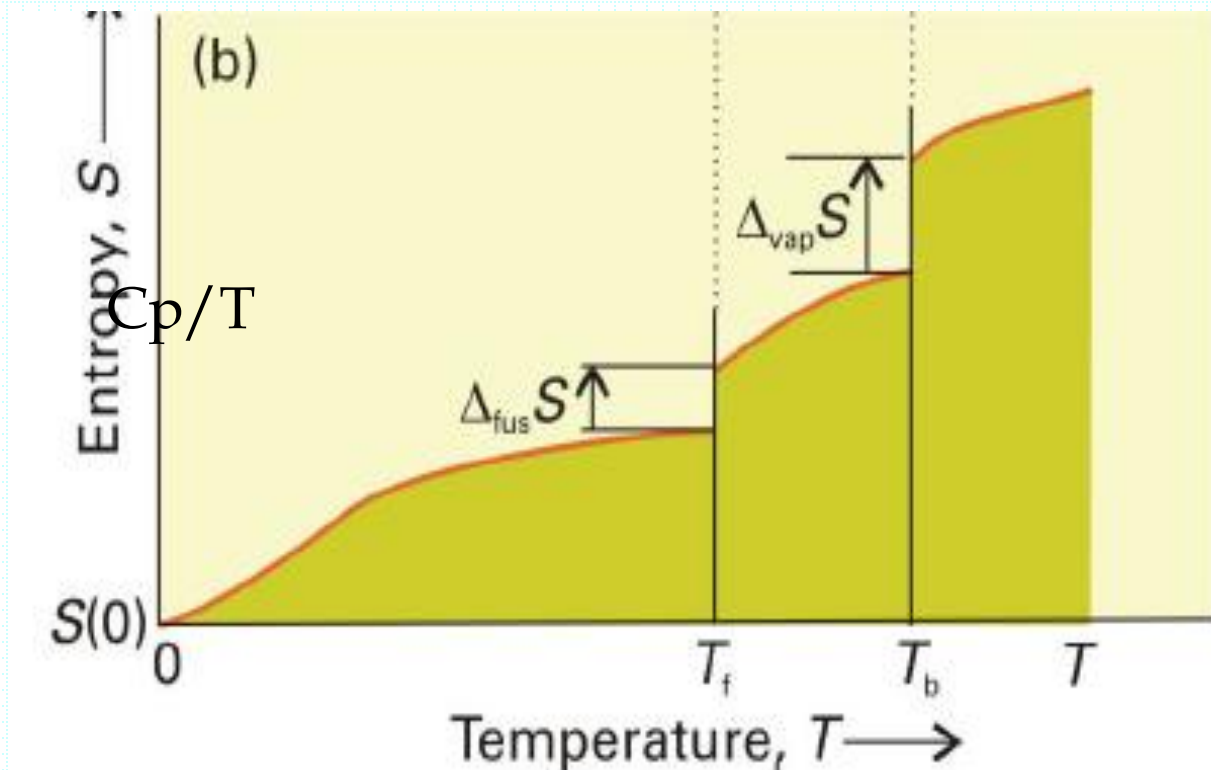
$$S_0 = 0$$

$$\text{Thus: } S_T = \Delta S_T$$

$$\begin{aligned} S(T) = S(0) &+ \int_0^{T_f} \frac{C_p(s)}{T} dT + \frac{\Delta H_{fus}}{T_f} \\ &+ \int_{T_f}^{T_b} \frac{C_p(l)}{T} dT + \frac{\Delta H_{vap}}{T_b} \\ &+ \int_{T_b}^T \frac{C_p(g)}{T} dT \end{aligned}$$

Absolute and standard molar entropies (S and S_m^0)

- Absolute entropies can be determined by integration of areas under **heat capacity/ T** as a function of T , and including entropies of phase transitions.
- Standard molar entropies are the molar entropies of substances at **1bar pressure** (and usually 298 K)



Standard molar entropies (@ 298K)

Substance	$S_m^\circ/\text{JK}^{-1}\text{mol}^{-1}$
Gases	
Ammonia, NH_3	192.5
Carbon dioxide, CO_2	213.7
Helium, He	126.2
Hydrogen, H_2	130.7
Neon, Ne	146.3
Nitrogen, N_2	191.6
Oxygen, O_2	205.1
Water vapour, H_2O	188.8
Liquids	
Benzene, C_6H_6	173.3
Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$	160.7
Water, H_2O	69.9

$$S_T^0 = \int_0^T \frac{C_P}{T} dT$$

$$S_{298}^0 = \int_0^{298} \frac{C_P}{T} dT$$

$$S_T^0 = S_{298}^0 + \int_{298K}^T \frac{C_P}{T} dT$$

Substance	$S_m^\circ/\text{JK}^{-1}\text{mol}^{-1}$
Solids	
Calcium oxide, CaO	39.8
Calcium carbonate, CaCO_3	92.9
Copper, Cu	33.2
Diamond, C	2.4
Graphite, C	5.7
Lead, Pb	64.8
Magnesium carbonate, MgCO_3	65.7
Magnesium oxide, MgO	26.9
Sodium chloride, NaCl	72.1
Sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$	360.2
Tin, Sn (white)	51.6
Sn (grey)	44.1

Standard reaction entropies

- Difference in molar entropy between products and reactants in their standard states is called the standard reaction entropy and can be expressed (like enthalpy) as:

$$\Delta_{\text{rxn}} S^{\circ} = \sum \nu S^{\circ}_{\text{m(products)}} - \sum \nu S^{\circ}_{\text{m(reactants)}}$$

- Note: absolute entropies, S , and standard molar entropies, S°_m , are discussed in section 4.7 of the textbook

Reaction Gibbs Free Energy

When the process is a reaction we talk about reaction Gibbs energy

Standard reaction Gibbs energy: $\Delta_r G^0$

$$\Delta_r G^0 = \sum_{\text{products}} \nu_p \Delta_f G^0(\text{products}) - \sum_{\text{reactants}} \nu_r \Delta_f G^0(\text{reactants})$$

Stoichiometric coefficients
in the chemical equation

Molar Gibbs formation
free energies

How to calculate $\Delta_r G^0$?

- From standard enthalpies and entropies of formation
- From standard Gibbs energies of formation

(we can see these values in tables)

Reaction Spontaneity & Temperature Changes

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

All of the four possible choices of signs for ΔH° and ΔS° give different temperature behaviors for ΔG° .

ΔH°	ΔS°	ΔG°	Description
—	+	—	Spontaneous at all T
+	—	+	Non-spontaneous at all T
—	—	+ or —	Spontaneous at low T; Non-spontaneous at high T
+	+	+ or —	Non-spontaneous at low T; Spontaneous at high T

Reaction Spontaneity & Temperature Changes

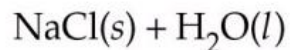
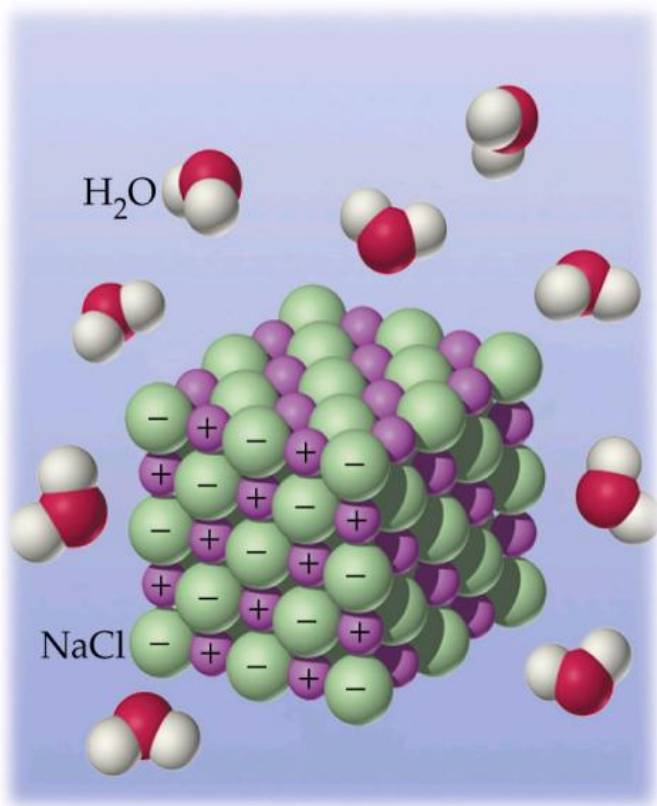
$$\Delta G = \Delta H - T\Delta S$$

TABLE 18.3 Factors Affecting the Sign of ΔG in the Relationship $\Delta G = \Delta H - T\Delta S$

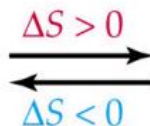
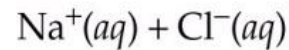
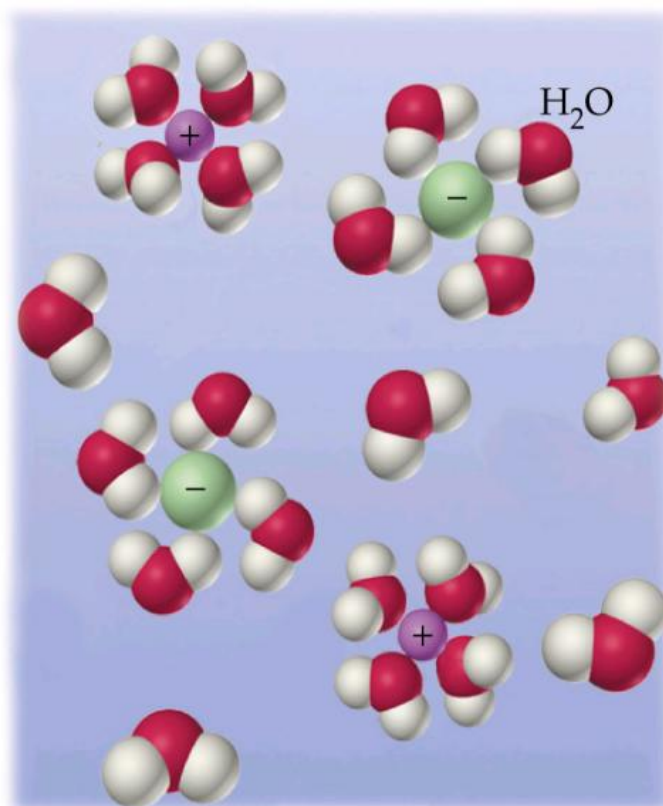
ΔH	ΔS	ΔG	Example	ΔG
+	+	Reaction proceeds spontaneously at high temperatures. At low temperatures, reaction is spontaneous in the reverse direction.	$2\text{HgO}(s) \longrightarrow 2\text{Hg}(l) + \text{O}_2(g)$	-ve
+	-	ΔG is always positive. Reaction is spontaneous in the reverse direction at all temperatures.	$3\text{O}_2(g) \longrightarrow 2\text{O}_3(g)$	+ve
-	+	ΔG is always negative. Reaction proceeds spontaneously at all temperatures.	$2\text{H}_2\text{O}_2(aq) \longrightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)$	-ve
-	-	Reaction proceeds spontaneously at low temperatures. At high temperatures, the reverse reaction becomes spontaneous.	$\text{NH}_3(g) + \text{HCl}(g) \longrightarrow \text{NH}_4\text{Cl}(s)$	-ve

Reaction Spontaneity & Temperature Changes

Less randomness
(less entropy)



More randomness
(more entropy)



Calculation of ΔG° at Various Temperatures

- | In this method you assume that ΔH° and ΔS° are essentially constant with respect to temperature.
- You get the value of ΔG_T° at any temperature T by substituting values of ΔH° and ΔS° at 25 °C into the following equation:

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

Exercise :

- | Find the ΔG° for the following reaction at 25°C and 1000°C. Relate this to reaction spontaneity.



ΔH_f° :	-1206.9	-635.1	-393.5 kJ
S° :	92.9	38.2	213.7 J/K

- | Place below each formula the values of ΔH_f° and S° multiplied by stoichiometric coefficients.

Calculation of ΔG° at Various Temperatures

$$\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

$$= [(-635.1 - 393.5) - (-1206.9)]\text{kJ} = 178.3\text{ kJ}$$

$$\Delta S^\circ = \sum n\Delta S^\circ(\text{products}) - \sum m\Delta S^\circ(\text{reactants})$$

$$= [(38.2 + 213.7) - (92.9)] = 159.0\text{ J / K}$$

- Now you substitute ΔH° , ΔS° ($=0.1590\text{ kJ/K}$), and T ($=298\text{K}$) into the equation for ΔG_f° .

$$\Delta G_T^\circ = 178.3\text{kJ} - (298\text{ K})(0.1590\text{ kJ / K})$$

$$\Delta G_T^\circ = 130.9\text{ kJ}$$

So the reaction is non-spontaneous at 25°C.

Calculation of ΔG° at Various Temperatures

- Now we'll use 1000°C (1273 K) along with our previous values for ΔH° and ΔS° .

$$\Delta G_T^\circ = -24.1 \text{ kJ}$$

So the reaction is **spontaneous** at 1000°C.

- To determine the minimal temperature for spontaneity, we can set $\Delta G_f^\circ = 0$ and solve for T.

$$T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

- To determine the minimal temperature for spontaneity, we can set $\Delta G_f^\circ = 0$ and solve for T.

$$T = \frac{178.3 \text{ kJ}}{0.1590 \text{ kJ/K}} = 1121 \text{ K } (848^\circ \text{C})$$