

MME 2009 Metallurgical Thermodynamics

Second law of thermodynamics

It is known from everyday life that nature does the most probable thing when nothing prevents that

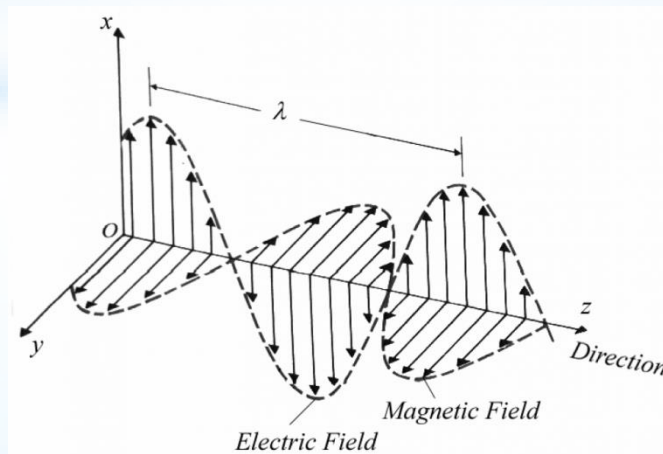
For example it rains at cool weather because the liquid phase has less energy and the reaction is exothermic

$$\Delta H^{\circ}_{\text{H}_2\text{O}(\text{g})} = -241.8 \text{ kJ/mole}, \Delta H^{\circ}_{\text{H}_2\text{O}(\text{l})} = -285.8 \text{ kJ/mole}$$

Enthalpy considerations explain only a part of the way nature behaves as water also evaporates at certain conditions although it is an endothermic reaction

The other part of the spontaneity discussions involve entropy, the degree of energy dispersion during a process

Enthalpy and entropy are extensive properties of matter that simultaneously determine the direction of a change in its energy, similar to the way electric and magnetic forces affect matter at the same time



The first law of thermodynamics states that total energy of the universe is constant and all processes that involve transfer of energy from one form to other can happen

The second law of thermodynamics restricts the processes that is considered possible by the first law to the most probable one that will happen under certain conditions set by the intensive properties of matter:

- The total entropy of any system plus that of its environment increases as a result of all natural processes
- The entropy of universe increases
- In all natural processes it has been found that the total entropy increases so natural processes tend to move toward a state of greater disorder.

In short, the entropy of the universe should increase as a result of a spontaneous process just happened



Alternative statements of the second law

- The entropy of a given system can increase or decrease but the change in entropy of the system ΔS , plus the change in entropy of the environment ΔS_{env} must be greater than or equal to zero
- It is impossible for an engine working in a cycle to transform a given amount of heat from a reservoir completely into work
- It is impossible to make a cyclic engine whose only effect is to transfer thermal energy from a colder body to a hotter body
- Heat can be completely converted into work in a single reversible process, but continuous conversion of heat into work requires a cyclic process (a heat engine)

Comparing energy, enthalpy and entropy

The total internal energy of the universe remains constant

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

The total heat energy of the universe increases as a result of irreversible processes

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

The total entropy of the universe increases

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

Therefore the total energy available in the universe to do work decreases as a result of irreversible processes

Entropy balance for matter undergoing a reversible process is

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$$

Entropy balance for an irreversible process

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

Thus entropy of universe constantly increases due to natural processes

Recall that

$$S_{surroundings} = \frac{-\Delta H_{system}}{T}$$

$$\Delta S_{universe} = \Delta S_{system} + \frac{-\Delta H_{system}}{T}$$

$$G_{system} = -T\Delta S_{universe} = \Delta H_{system} - T\Delta S_{system}$$

Any process that results in a decrease in the total Gibbs free energy of the system is spontaneous

$$G_{system} = \Delta H_{system} - T\Delta S_{system} < 0$$

Enthalpy of a system is the energy of the system at constant temperature and pressure

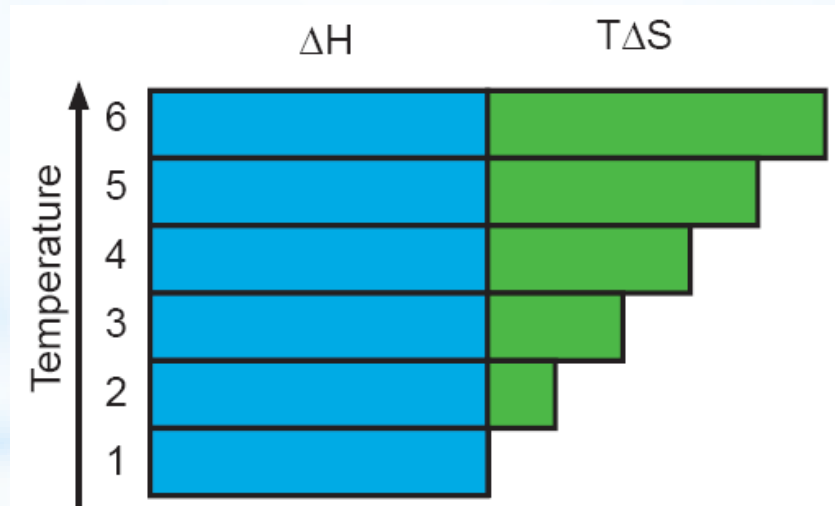
However not all of that energy is available for the system to do work or contribute to a chemical reaction

Recall that

$$H = U + PV$$

Entropy times temperature is not an energy but it controls the availability of energy to do work

Consider the change in energy content of a process with temperature:

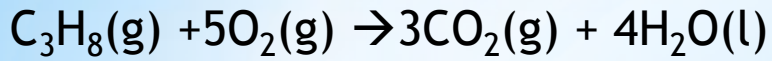


The process will happen irreversibly when temperature exceeds T_6 where the process is in equilibrium

$$G = \Delta H - T\Delta S = 0$$

Equilibrium condition

Example - Consider the combustion of propane to form CO₂ and H₂O at 298 K:

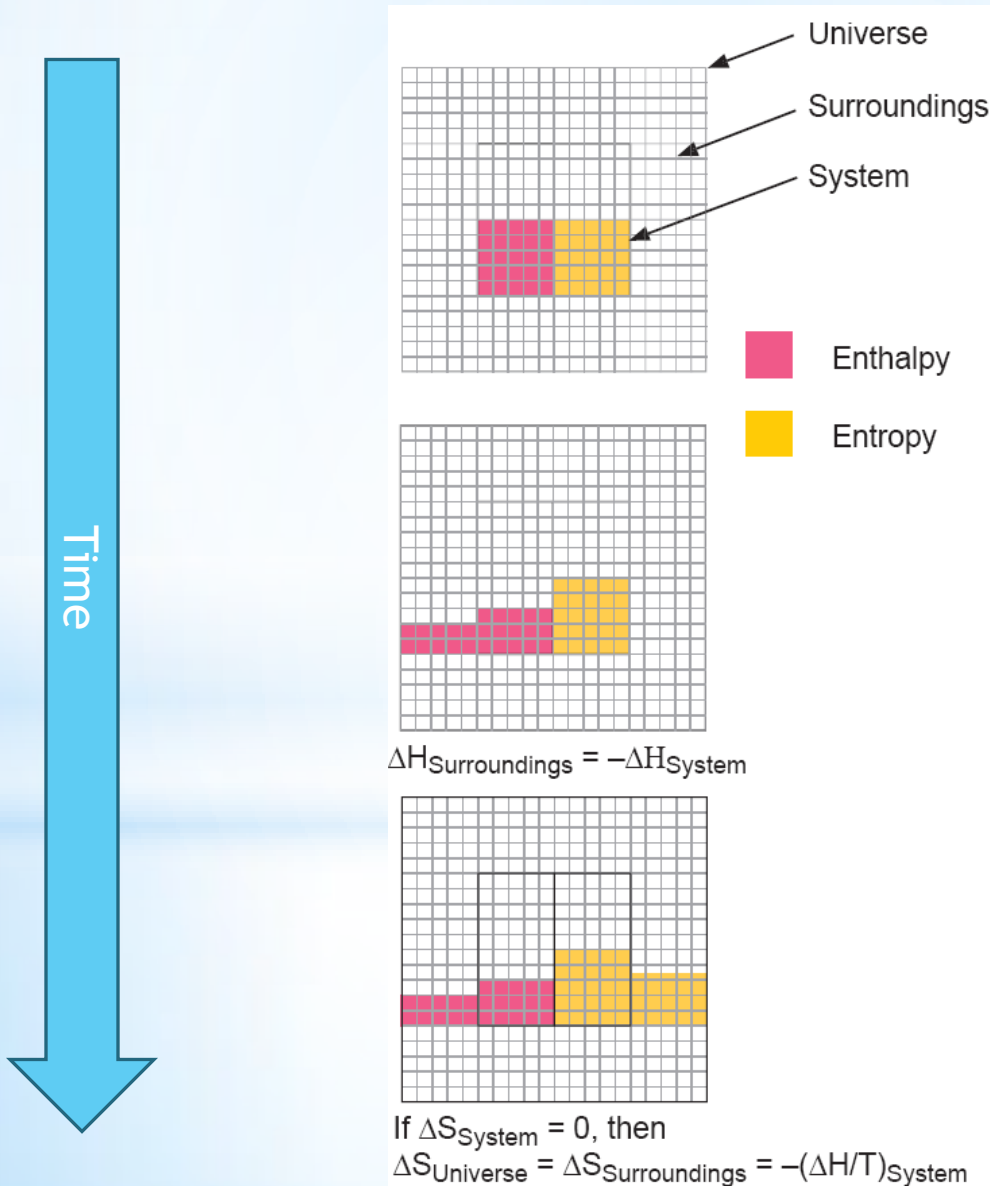


At what temperature does the reverse reaction become spontaneous?

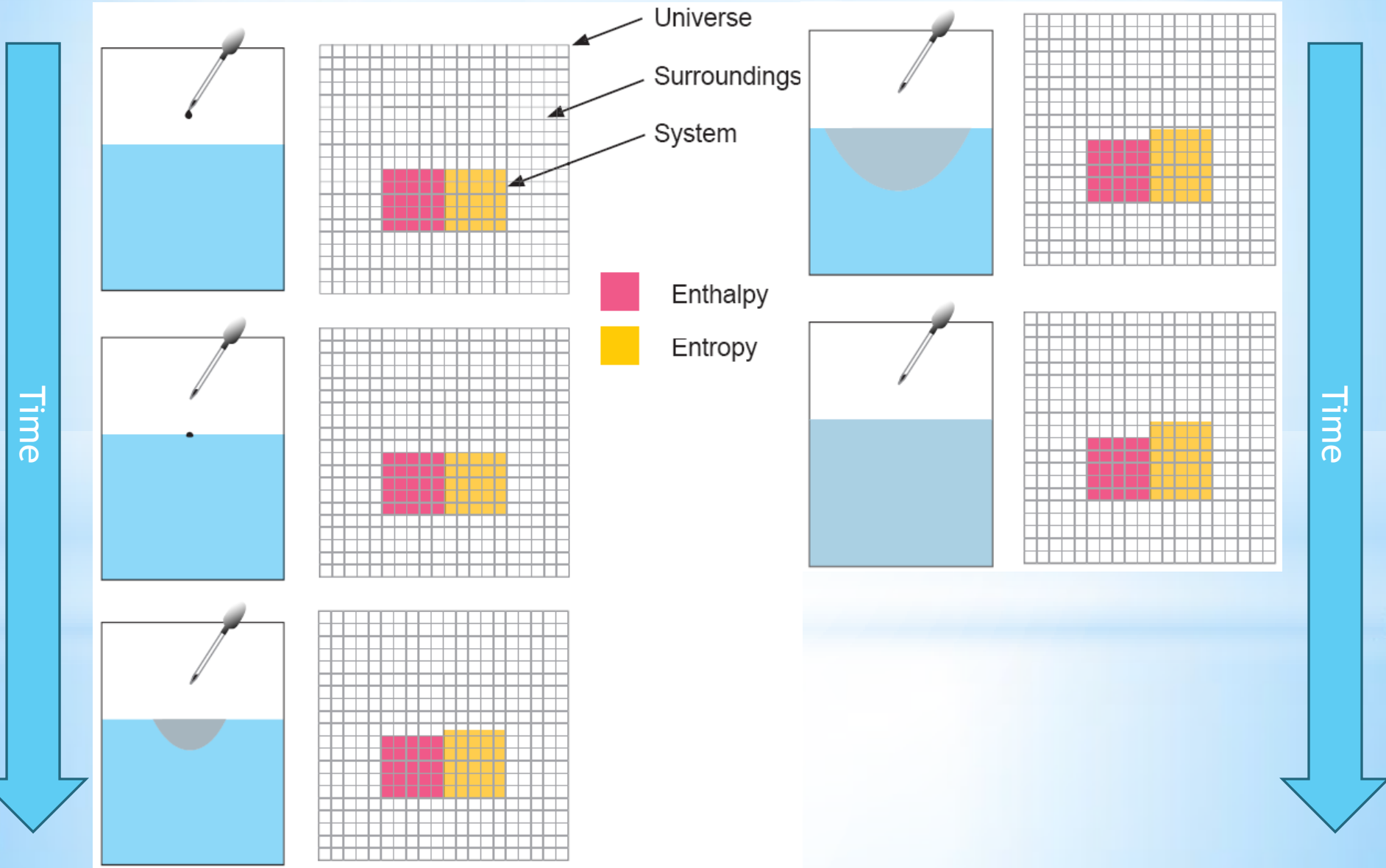
$\Delta H = -248.5 \text{ kJ}$; and $\Delta S = -184.1 \text{ J/K}$ at 298 K

Spontaneous dispersion of heat energy and the resultant increase in entropy

The energy transfer between an open system and the surroundings



Spontaneous diffusion of molecules in the system and the resultant increase in entropy

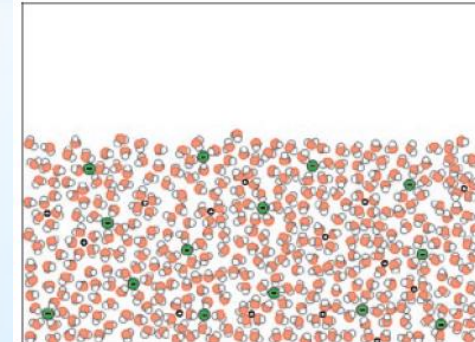
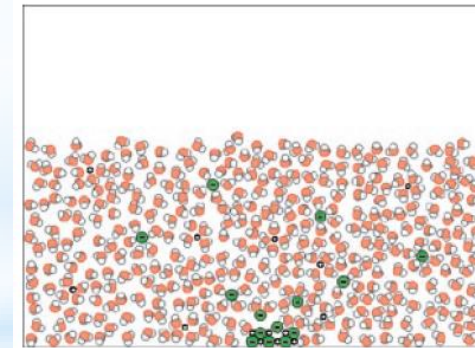
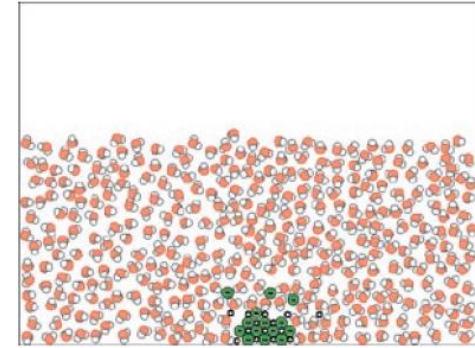
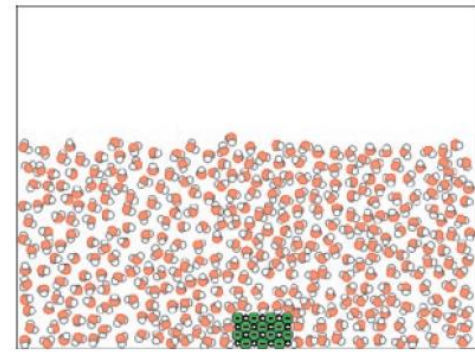
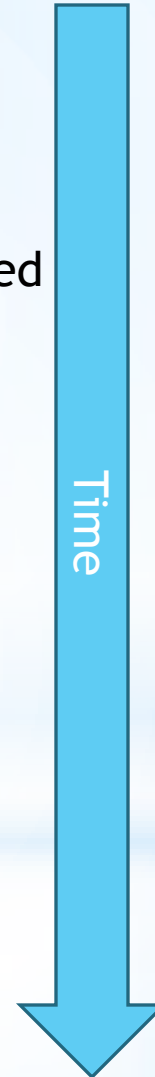


Salt dissolving in water

Solutions of comparable concentrations of species are complex such that the components interact with each other

Entropy has dual effect upon salt dissolution in water:

- 1- Entropy is increased by the additional space occupied by the salt ions
- 2- Entropy is decreased by the orientation of water molecules around salt ions



Gibbs free energy and reaction spontaneity

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

ΔG = Gibbs free energy (kJ/mole)
 ΔH = Enthalpy change (kJ/mole)
 ΔS = Entropy change (J/mole.K)
T = Kelvin temperature (always +)

If ΔS for a reaction is (+), reaction is favored due to higher freedom of the products

If ΔH is (-), reaction is favored due to lower energy of the products

so

$$\Delta G = (-) - (+) (+) = (-)$$

since both entropy and enthalpy drive the reaction forward, the reaction must be spontaneous forward

Thus a negative ΔG indicates a spontaneous forward reaction

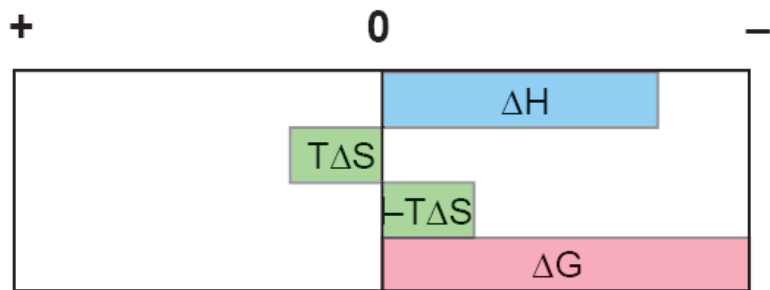
$\Delta G = -$ \longrightarrow Forward reaction is spontaneous

$\Delta G = +$ \longleftarrow Reverse reaction is spontaneous

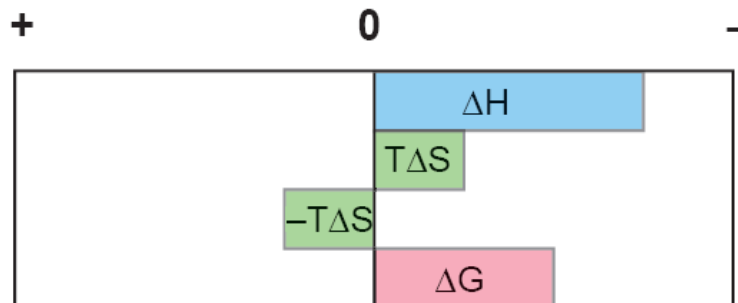
$\Delta G = 0$ \longrightarrow Reaction is at equilibrium

Four possible sign combinations for Gibbs free energy

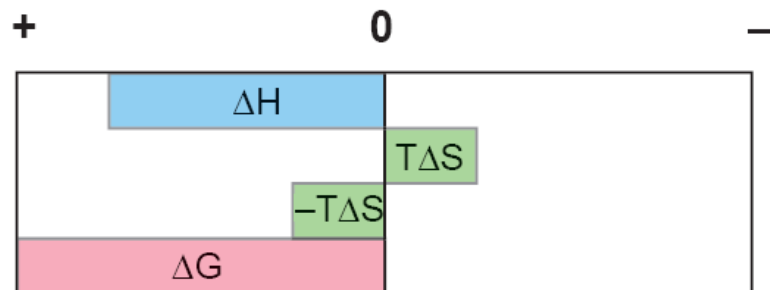
REACTION TYPE ONE



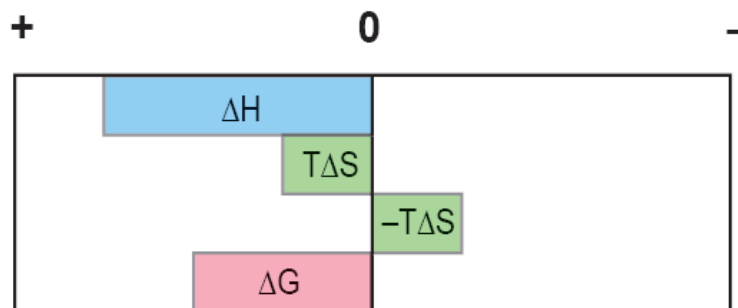
REACTION TYPE THREE



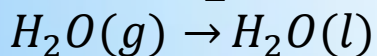
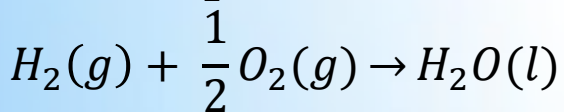
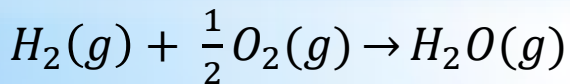
REACTION TYPE TWO



REACTION TYPE FOUR



Example - Which reaction type do the following reactions fit into ?



$$\Delta H^\circ_{H_2O(g)} = -241.8 \text{ kJ/mole}$$

$$\Delta H^\circ_{H_2O(l)} = -285.8 \text{ kJ/mole}$$

TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

Substance	S° , J/mol-K
Gases	
H ₂ (g)	130.6
N ₂ (g)	191.5
O ₂ (g)	205.0
H ₂ O(g)	188.8
NH ₃ (g)	192.5
CH ₃ OH(g)	237.6
C ₆ H ₆ (g)	269.2
Liquids	
H ₂ O(l)	69.9
CH ₃ OH(l)	126.8
C ₆ H ₆ (l)	172.8
Solids	
Li(s)	29.1
Na(s)	51.4
K(s)	64.7
Fe(s)	27.23
FeCl ₃ (s)	142.3
NaCl(s)	72.3

Gibbs free energy varies strongly with temperature

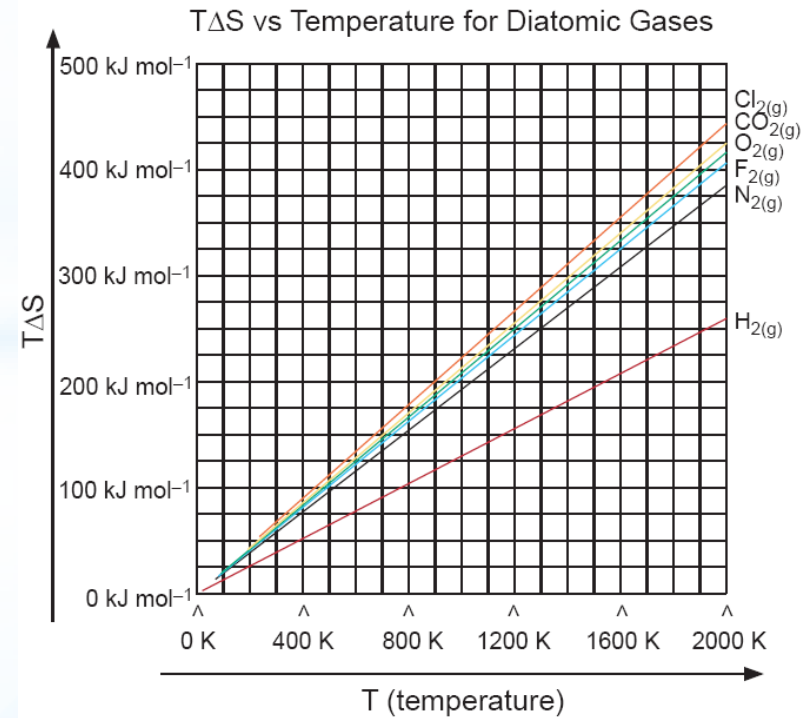
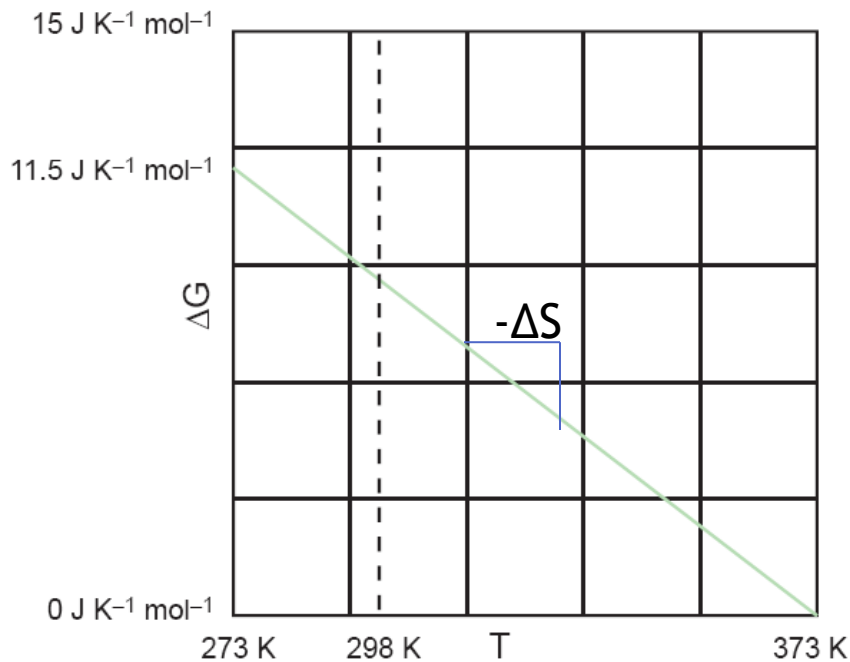
Consider the evaporation of water $H_2O(l) \rightarrow H_2O(g)$

$$\Delta H = 44 \text{ kJ/mole at } 298 \text{ K}$$

$$\Delta S = 119 \text{ J/mole.K at } 298 \text{ K}$$

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

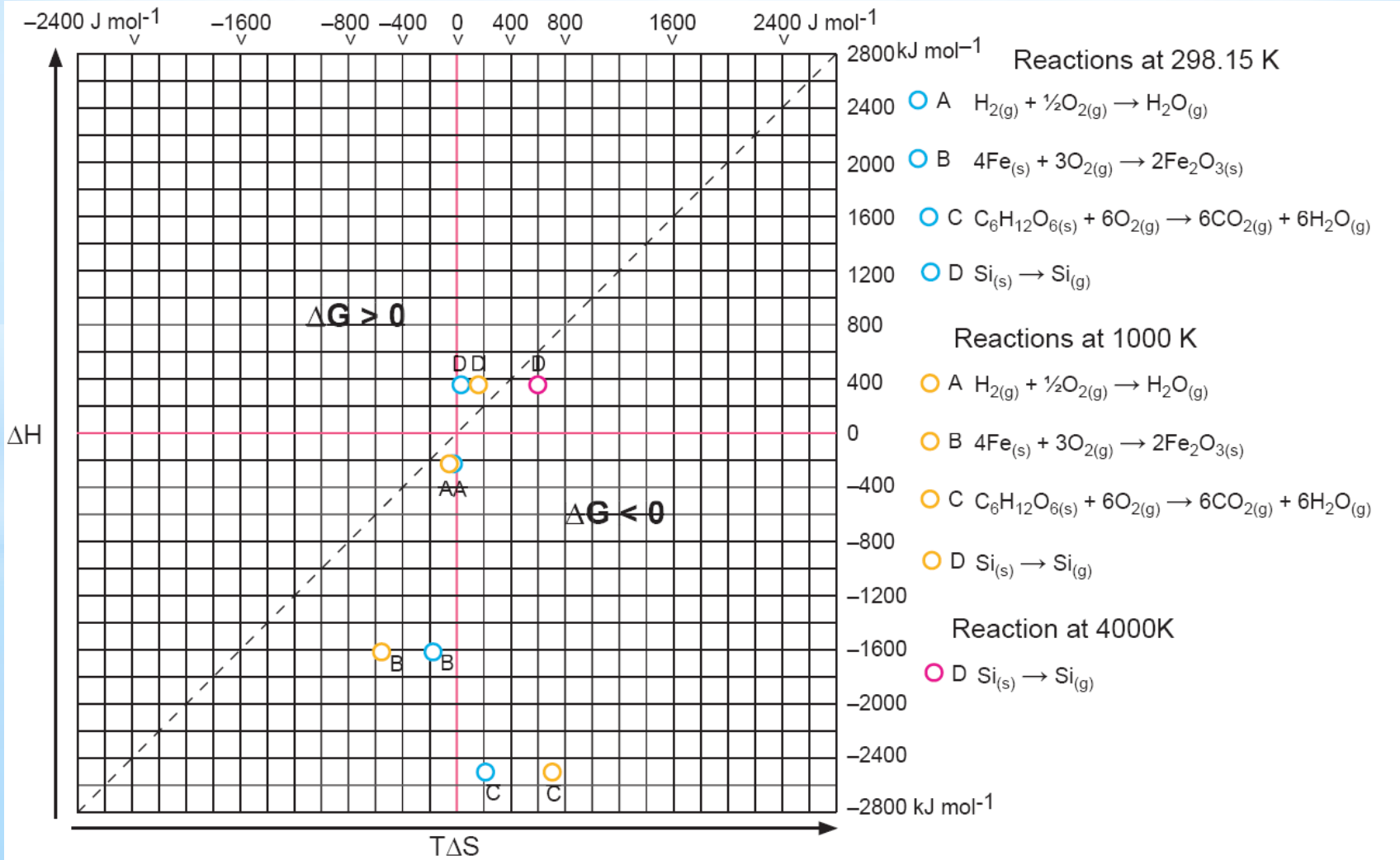
The following dependence of Gibbs free energy on temperature is seen if the enthalpy and entropy values of water are taken constant in the temperature range $298 < T < 373 \text{ K}$



The effect of temperature on spontaneity is most strongly observed when enthalpy and entropy are of the same sign

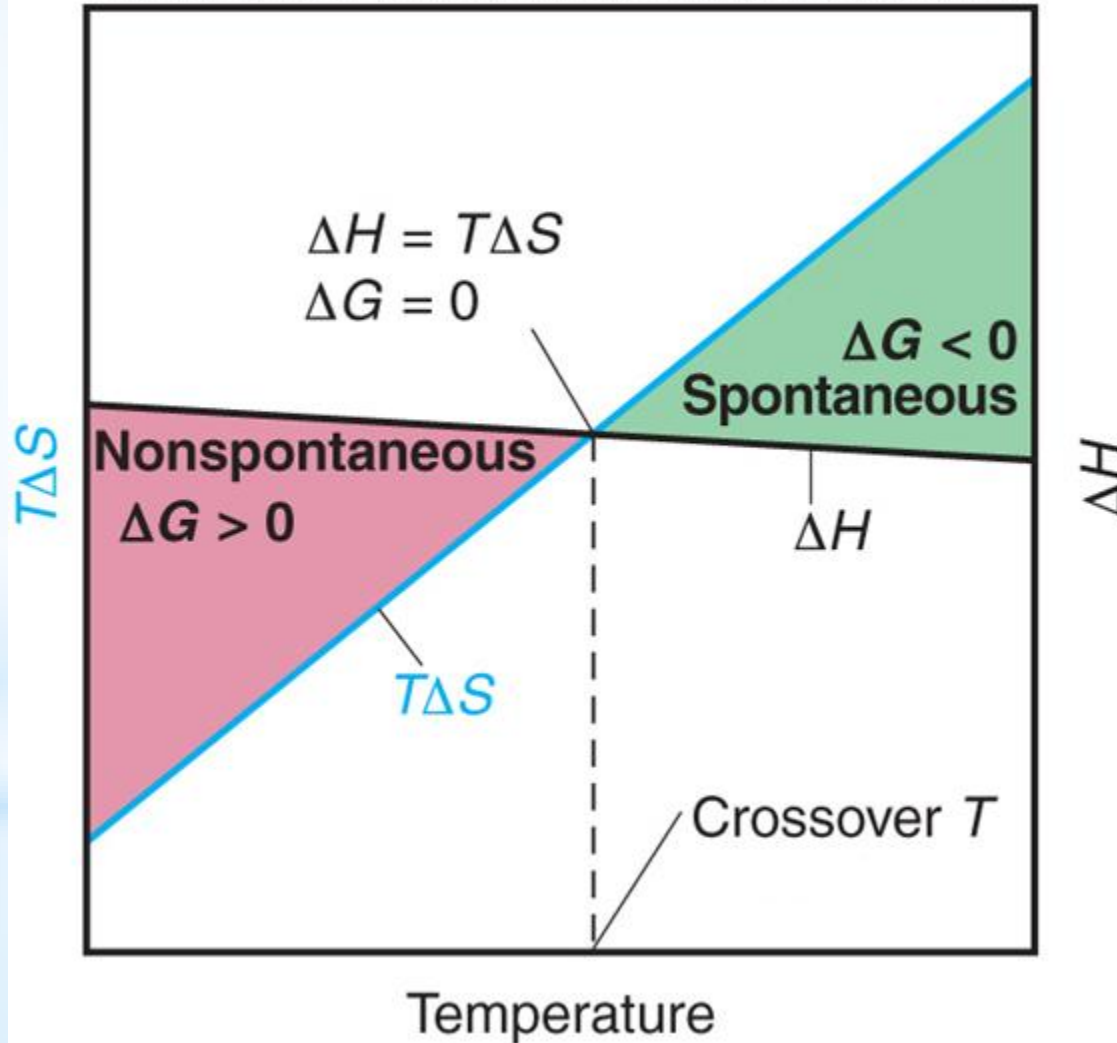
In this case when enthalpy and entropy factors affect Gibbs free energy oppositely,

- entropy factor $T\Delta S$ dominates at high temperatures
- enthalpy factor ΔH dominates at low temperatures



The sign of ΔG changes at $T = \frac{\Delta H}{\Delta S}$

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Example - Oxidation of $\text{SO}_2(\text{g})$ to $\text{SO}_3(\text{g})$ happens during the production of sulfuric acid according to the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$

$\Delta G = -141.6 \text{ kJ}$; $\Delta H = -198.4 \text{ kJ}$; and $\Delta S = -187.9 \text{ J/K}$ at 298 K

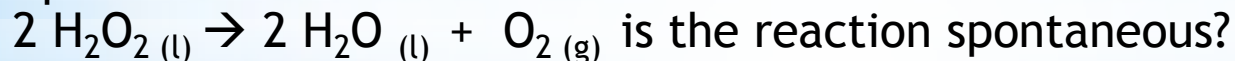
Find out if this reaction is spontaneous at 25°C , and predict how ΔG will change with increasing T

Deciding on reaction spontaneity without calculation

The signs of ΔH , ΔS and ΔG can be used to decide on the spontaneity of reactions as well as the temperature dependence of a reaction

ΔH	T_K	ΔS	ΔG	Reaction Direction
-	+	+	-	SPONTANEOUS AT ALL TEMPERATURES
+	+	-	+	NON SPONTANEOUS AT ALL TEMPERATURES
-	+	-	+ / -	SPONTANEOUS AT LOW TEMPERATURES
+	+	+	+ / -	SPONTANEOUS AT HIGH TEMPERATURES

Example: If $\Delta H = -46.9$ Kcal for the reaction:



Since ΔH is temperature independent, the reaction is exothermic at all temperatures and is favored by lower energy

Two liquid molecules convert to two liquid and a gas molecule and is therefore favored by increasing entropy

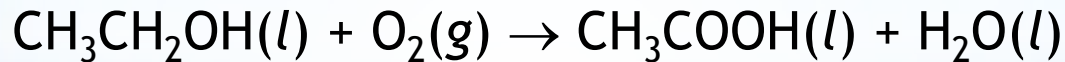
Both lower enthalpy (ΔH is negative) and increasing entropy (ΔS is positive) favor the forward reaction and the reaction is sure to be spontaneous at all temperatures

The standard Gibbs free energy of formation is the free energy change that occurs when 1 mole of substance is formed from its elements in their standard states at 1 atm and at 298 K

The corresponding reaction for the standard Gibbs free energy of formation is the same as that for standard enthalpy of formation, ΔH°

$$\Delta G^\circ = \sum n \Delta G^\circ_{\text{products}} - \sum m \Delta G^\circ_{\text{reactants}}$$

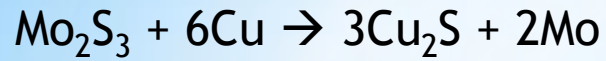
Example - Calculate the change in Gibbs free energy, ΔG° for the oxidation of ethyl alcohol to acetic acid using standard free energies of formation



ΔG° , kJ/mol	-174.8	0	-392.5	-237.2
n , mol	1	1	1	1
$n\Delta G^\circ$, kJ	-174.8	0	-392.5	-237.2

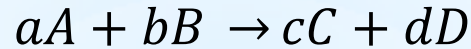
$$\Delta G^\circ = -629.7 - (-174.8) = -454.9 \text{ kJ}$$

Example - Will this reaction occur spontaneously at 298 K?



Data	ΔH°_{298}	S°_{298}	a	b	c
Cu(s)	0	33.36	22.6	6.3	
Cu ₂ S(s)	-82000	119.59	81.63		
Mo(s)	0	28.59	22.94	5.44	
Mo ₂ S ₃ (s)	-386650	119.13	126.3	-26.92	

Consider a general reaction in equilibrium:



The general criterion for equilibrium under constant T and P is $\Delta G = 0$

$$\begin{aligned}\Delta G &= \sum G_{products} - \sum G_{reactants} \\ &= cG_C + dG_D - aG_A - bG_B\end{aligned}$$

The complete differential of G in terms of T and P is

$$\begin{aligned}dG &= \left(\frac{\partial G}{\partial P}\right) dP + \left(\frac{\partial G}{\partial T}\right) dT \\ dG &= VdP - SdT\end{aligned}$$

Consider the reaction in a mixture of ideal gases at constant temperature

The change in Gibbs free energy of each ideal gas component as a function of its pressure is given as

$$\begin{aligned}\frac{\partial G_i}{\partial P_i} &= V \\ dG_i &= \frac{RTdP_i}{P_i}\end{aligned}$$

$$\int dG_i = \int \frac{RT dP_i}{P_i}$$

$$G_i = G_i^o + RT \ln \frac{P_i}{P_i^o} = G_i^o + RT \ln a_i$$

The change in free energy of the system at constant temperature is

$$nG = \sum n_i G_i$$

$$d(nG) = \sum n_i dG_i + \sum G_i dn_i$$

$$\Delta(nG) = \sum \frac{RTn_i}{P_i} dP_i + \sum G_i dn_i$$

Since mole number and pressure of ideal gases are proportional, n_i / P_i is constant

and since the total pressure of the system is constant, $\sum dP_i = 0$

$$\Delta G = \sum G_i dn_i$$

In the case of system equilibrium

$$\Delta G = \sum G_i dn_i = 0$$

$$\Delta G = \sum G_i^{\circ} dn_i + RT \sum \ln(P_i dn_i)$$

If the number of molecules of each component in the ideal gas mixture is relatively high, their coefficients a , b , c , d can be used to represent dn_i :

$$cG_C^{\circ} + dG_D^{\circ} - aG_A^{\circ} - bG_B^{\circ} + RT \ln P_C^c + RT \ln P_D^d + RT \ln P_A^{-a} + RT \ln P_B^{-b} = 0$$

$$\Delta G^{\circ} + RT \ln \frac{P_C^c P_D^d}{P_A^a P_B^b} = 0$$

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

Absolute Gibbs free energy is computed for condensed phases as:

$G_i = G_i^{\circ} + RT \ln a_i$ where a can be taken as unity for pure condensed phases

The equation for condensed phases can be written as

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

Q is called the reaction quotient

Q = K when $\Delta G = 0$

$$\Delta G = 0 = \Delta G^{\circ} + RT \ln K$$

ΔG° is readily given in literature for most compounds at STP

ΔG° can be calculated for any temperature, since $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

$$\Delta G^{\circ} = \Delta H^{\circ}_{298} + \int_{298}^T \Delta C_P dT - T \left(\Delta S^{\circ}_{298} + \int_{298}^T \frac{\Delta C_P dT}{T} \right)$$

where $C_P = a + bT + \frac{c}{T^2}$


and $\Delta C_P = \Delta a + \Delta bT + \frac{\Delta c}{T^2}$ where $\Delta a, b, c = \sum \Delta a, b, c_{products} - \sum \Delta a, b, c_{reactants}$

ΔG° is the free energy change that would accompany the complete conversion of all reactants, initially present in their standard states, to all products in their standard states

ΔG is the free energy change for other temperatures and pressures

The relationship between ΔG° and K at 298 K

ΔG° (kJ)	K	Significance
200	9×10^{-36}	Essentially no forward reaction; reverse reaction goes to completion
100	3×10^{-18}	
50	2×10^{-9}	
10	2×10^{-2}	
1	7×10^{-1}	
0	1	Forward and reverse reactions proceed to same extent
-1	1.5	
-10	5×10^1	
-50	6×10^8	
-100	3×10^{17}	Forward reaction goes to completion; essentially no reverse reaction
-200	1×10^{35}	



Example - Estimate ΔG° for the decomposition of NO_2 at 25°C
At 25°C and 1.00 atmosphere pressure, $K = 4.3 \times 10^{-13}$

$$\Delta G = RT \ln Q - RT \ln K = RT \ln \frac{Q}{K}$$

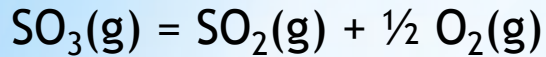
ΔG has a very large positive or negative value if Q and K are very different

The reaction releases or absorbs a large amount of free energy

ΔG has a very small positive or negative value if Q and K are close

The reaction releases or absorbs a small amount of free energy

Example -The equilibrium constant at different temperatures for the following reaction is given:



$$K = 0.146 \quad @ \quad 900\text{K}$$

$$K = 0.516 \quad @ \quad 1000\text{K}$$

$$K = 1.45 \quad @ \quad 1100\text{K}$$

Estimate the enthalpy change of the reaction at 1000K and the equilibrium composition at the same temperature