

# Engineering Thermodynamics

Second law of thermodynamics

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

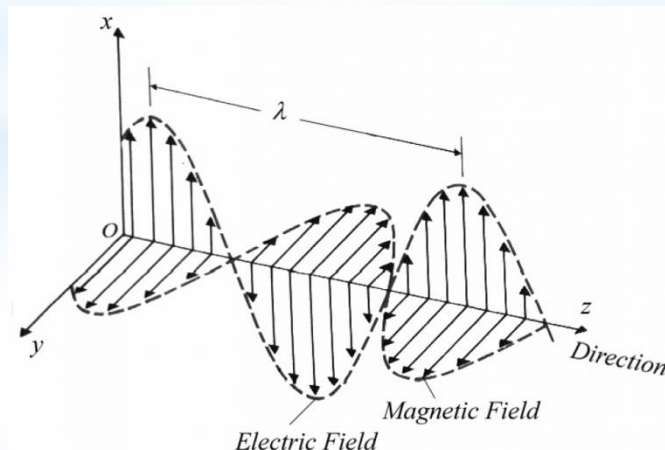
For example it rains at cool weather because the liquid phase has less energy and the reaction is exothermic

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

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 state 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



## Alternative statements of the second law

- The entropy of a given system can increase or decrease but the change in entropy of the system  $\Delta S$ , plus the change in entropy of the environment  $\Delta S_{\text{surr}}$  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 theoretically 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

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

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

The ultimate criterion for spontaneity of a process is that the entropy of the universe should increase

$$\Delta S_{universe} = \Delta S_{system} + \frac{-\Delta H_{system}}{T} > 0$$

Multiplying both sides by -T gives the spontaneity equation:

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

$$T\Delta S_{universe} > 0$$

$-T\Delta S_{universe}$  is called the **Gibbs free energy of the system**

For a process to be spontaneous, entropy of the universe should increase and Gibbs free energy of the system should decrease

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

Internal energy of a system transferring energy to the surroundings decreases

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

$$\Delta H - P\Delta V = \Delta U = 0$$

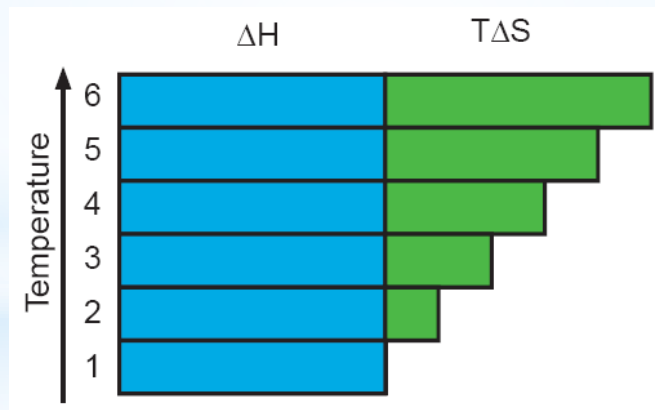
Not all of internal energy is available for the system to do work or contribute to a chemical reaction

Entropy times temperature controls the availability of energy to do work (expansion, phase change, chemical reaction)

Consider the change in energy content of a process with temperature

$\text{NH}_4\text{Cl(s)}$  is placed in an adiabatic cylinder with a piston and work is obtained as the following reaction takes place  $\text{NH}_4\text{Cl(s)} \Rightarrow \text{NH}_3\text{(g)} + \text{HCl(g)}$   $\Delta S = 284 \text{ J/mole.K}$

$$\Delta H = 176000 \text{ J/mole}$$

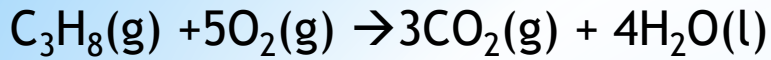


$$\Delta G = \Delta H - T_6 \Delta S = 0$$

Equilibrium condition

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

Example - Consider the combustion of propane to form CO<sub>2</sub> and H<sub>2</sub>O at 298 K:



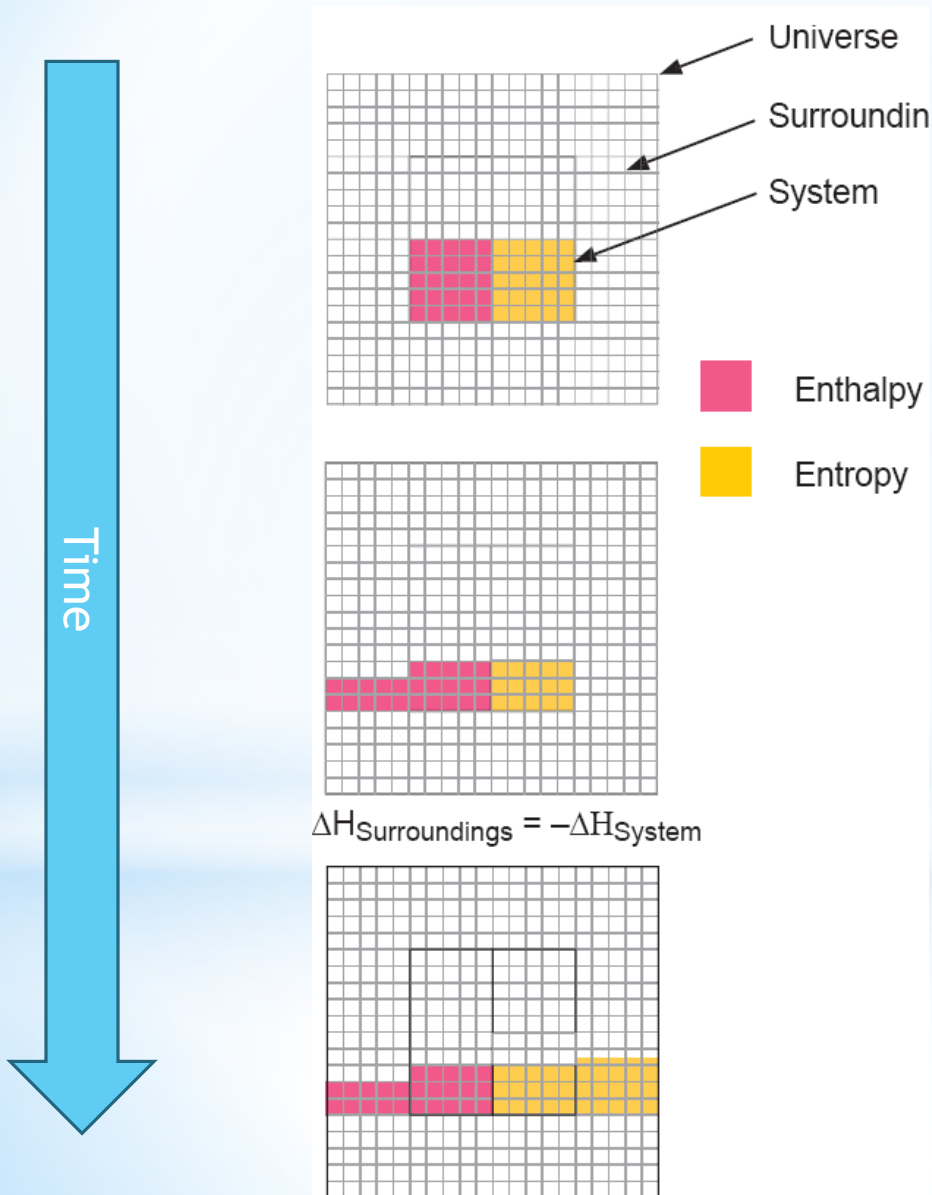
If the  $\Delta C_p$  calculated according to the Kirschhof's law is about zero, at what temperature does the reverse reaction become spontaneous?

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

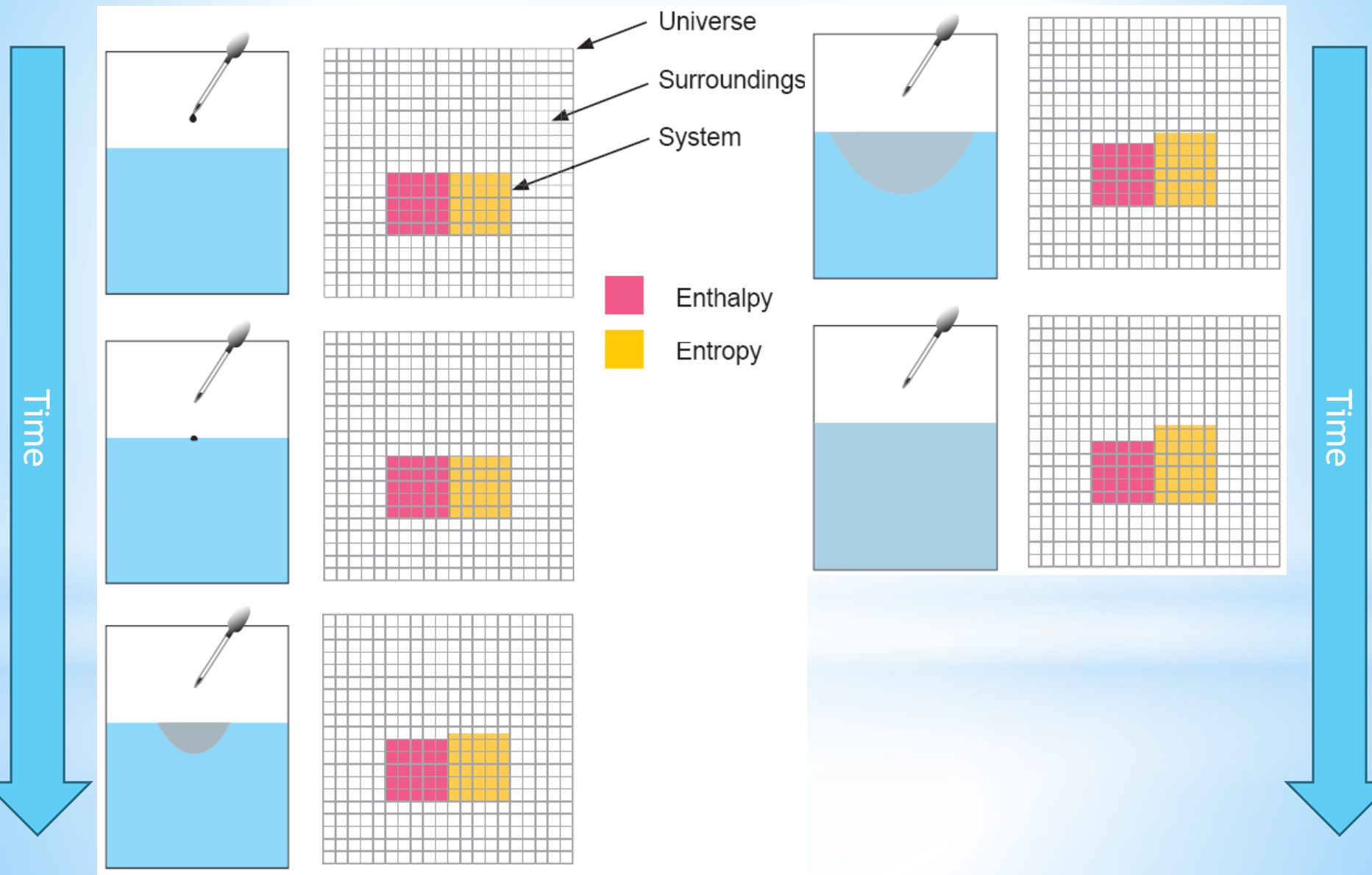


# Spontaneous dispersion of heat energy and the resultant increase in entropy

The energy transfer between an open system and the surroundings



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

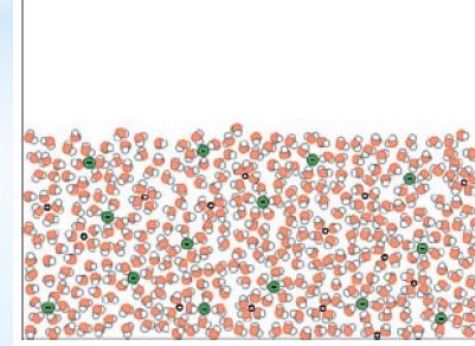
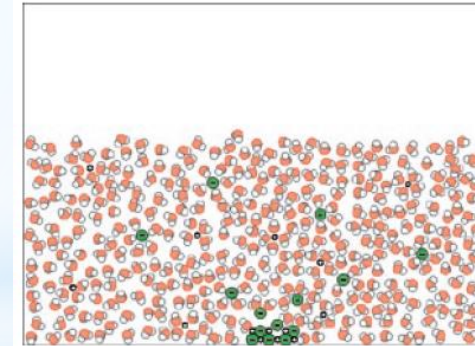
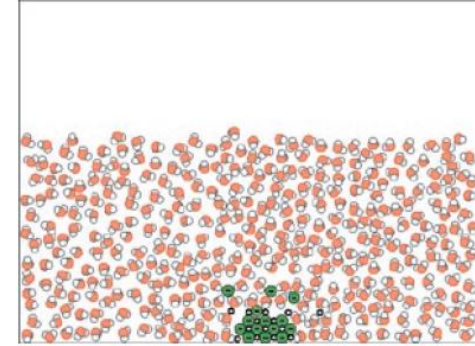
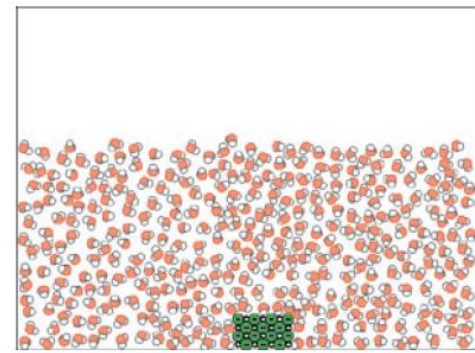
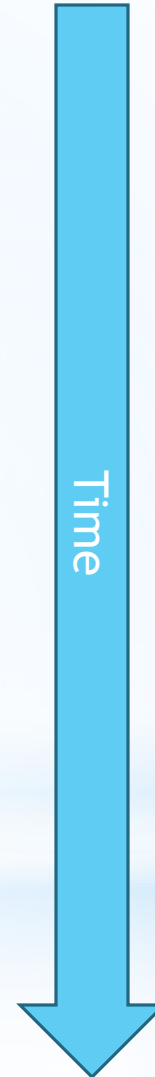


# Salt dissolving in water

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



## Reaction spontaneity and Gibbs free energy

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

$\Delta G$  = Gibbs free energy (kJ/mole)  
 $\Delta H$  = Enthalpy change (kJ/mole)  
 $\Delta S$  = Entropy change (J/mole.K)  
T = Kelvin temperature (always +)

If  $\Delta S$  for a reaction is (+), forward reaction is favored due to higher freedom of the products

If  $\Delta H$  is (-), forward 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  $\Delta G$  indicates a spontaneous forward reaction

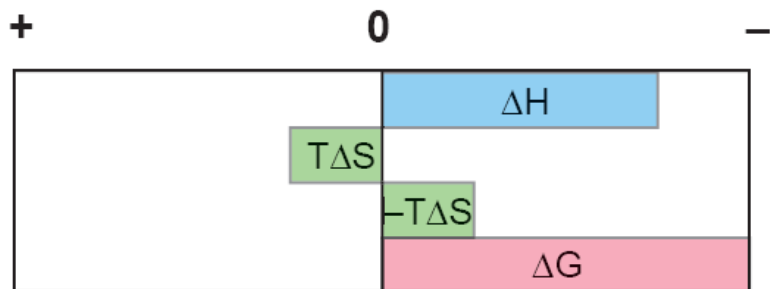
$\Delta G = -$   $\longrightarrow$  Forward reaction is spontaneous

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

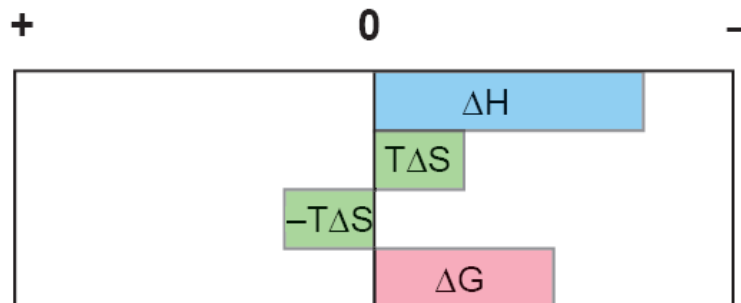
$\Delta G = 0$   $\longdashrightarrow$  Reaction is at equilibrium

# Four possible sign combinations for Gibbs free energy

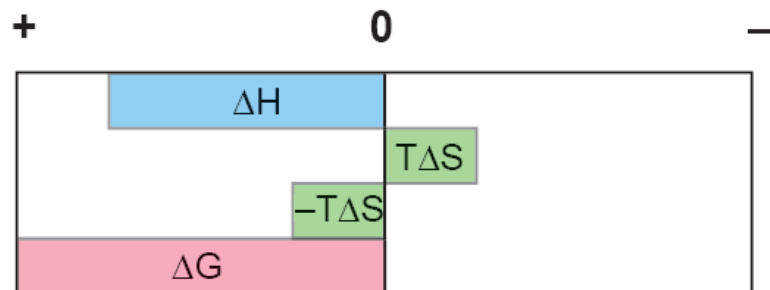
REACTION TYPE ONE



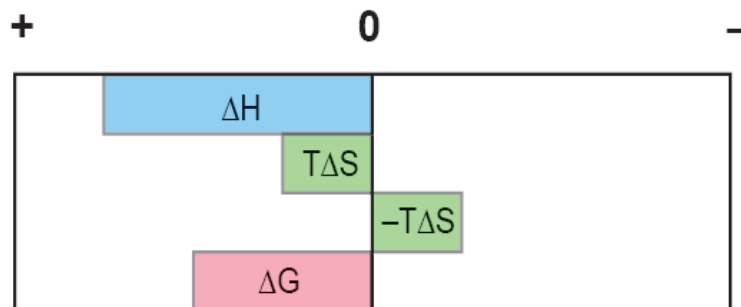
REACTION TYPE THREE



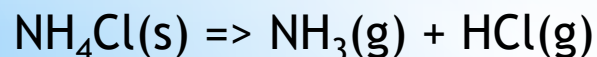
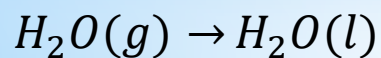
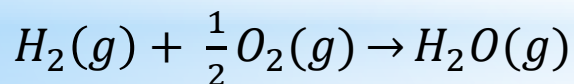
REACTION TYPE TWO



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	$S^\circ$ , J/mol-K
<b>Gases</b>	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
<b>Liquids</b>	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
<b>Solids</b>	
$Li(s)$	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

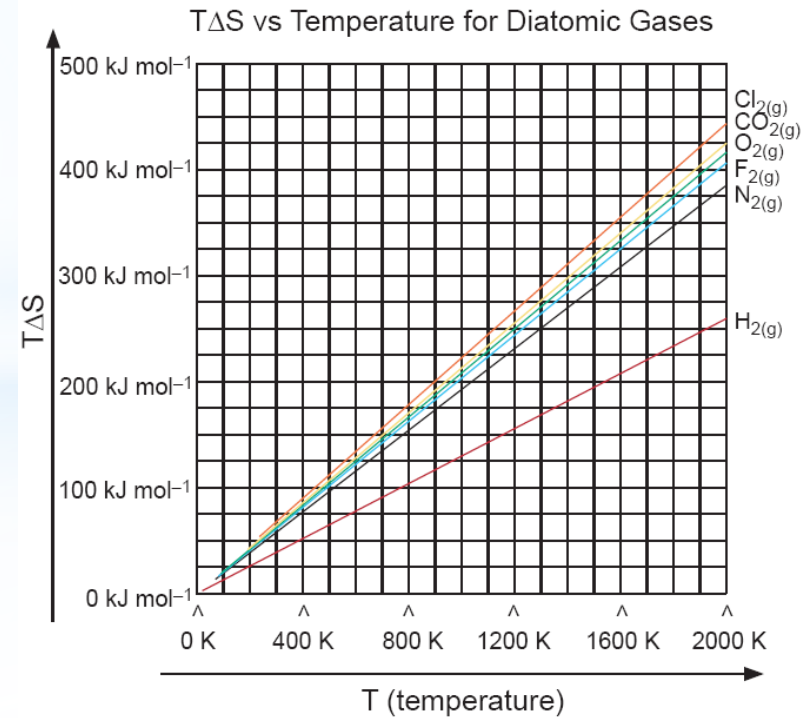
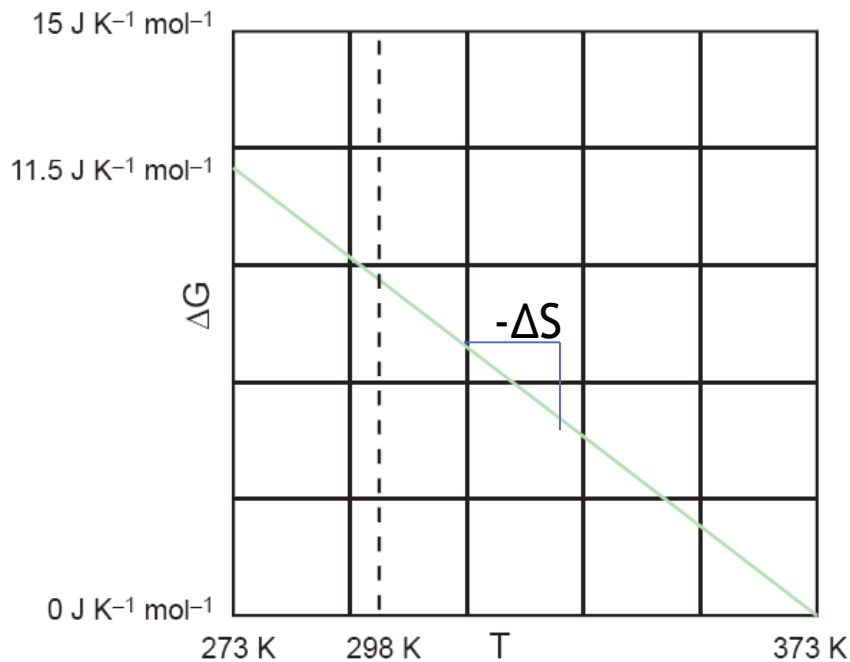
Consider the evaporation of water  $H_2O(l) \rightarrow H_2O(g)$

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

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

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

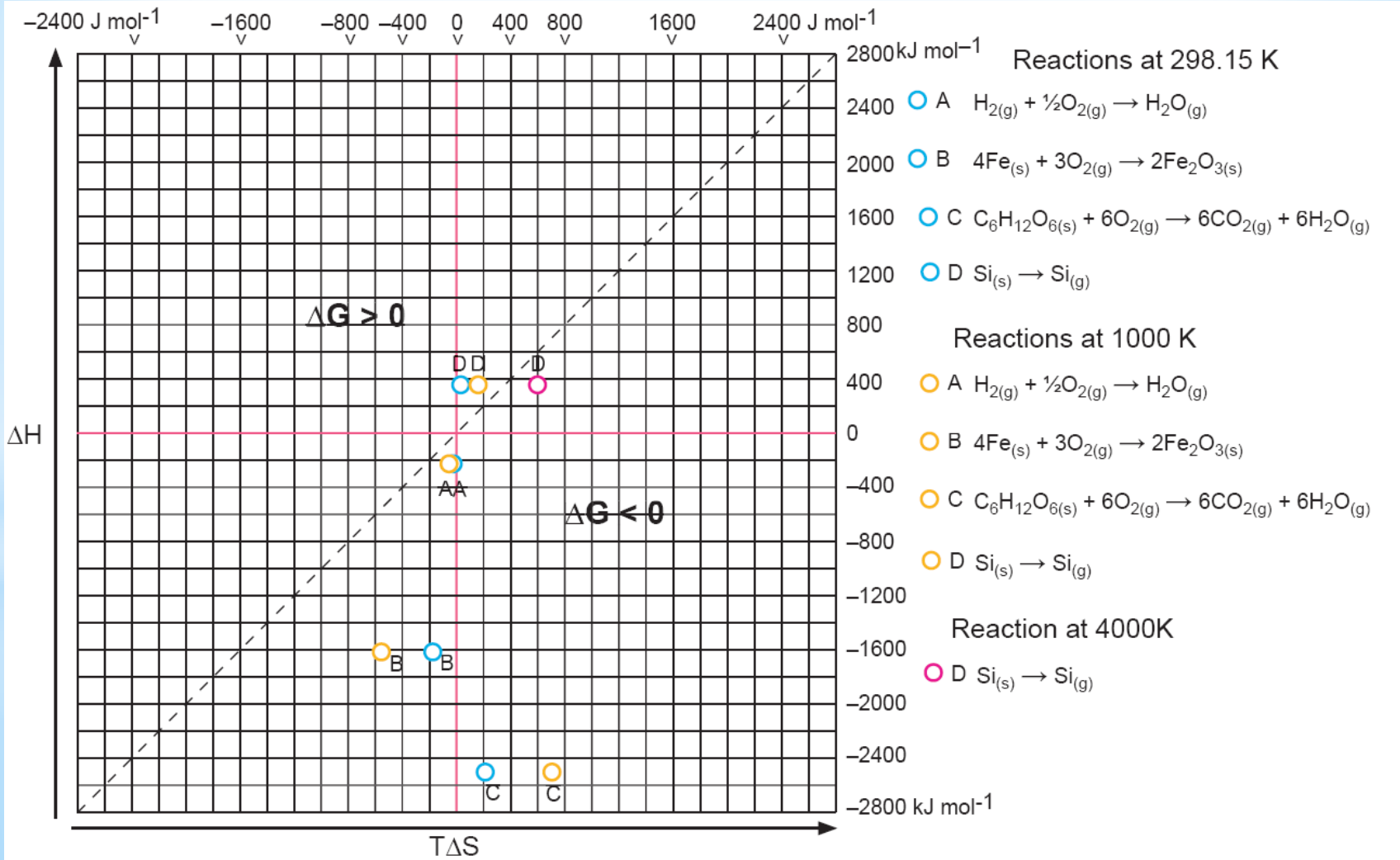
The following dependence of Gibbs free energy on temperature is seen if the enthalpy and entropy values of water are taken constant in the temperature range  $298 < T < 373 \text{ K}$



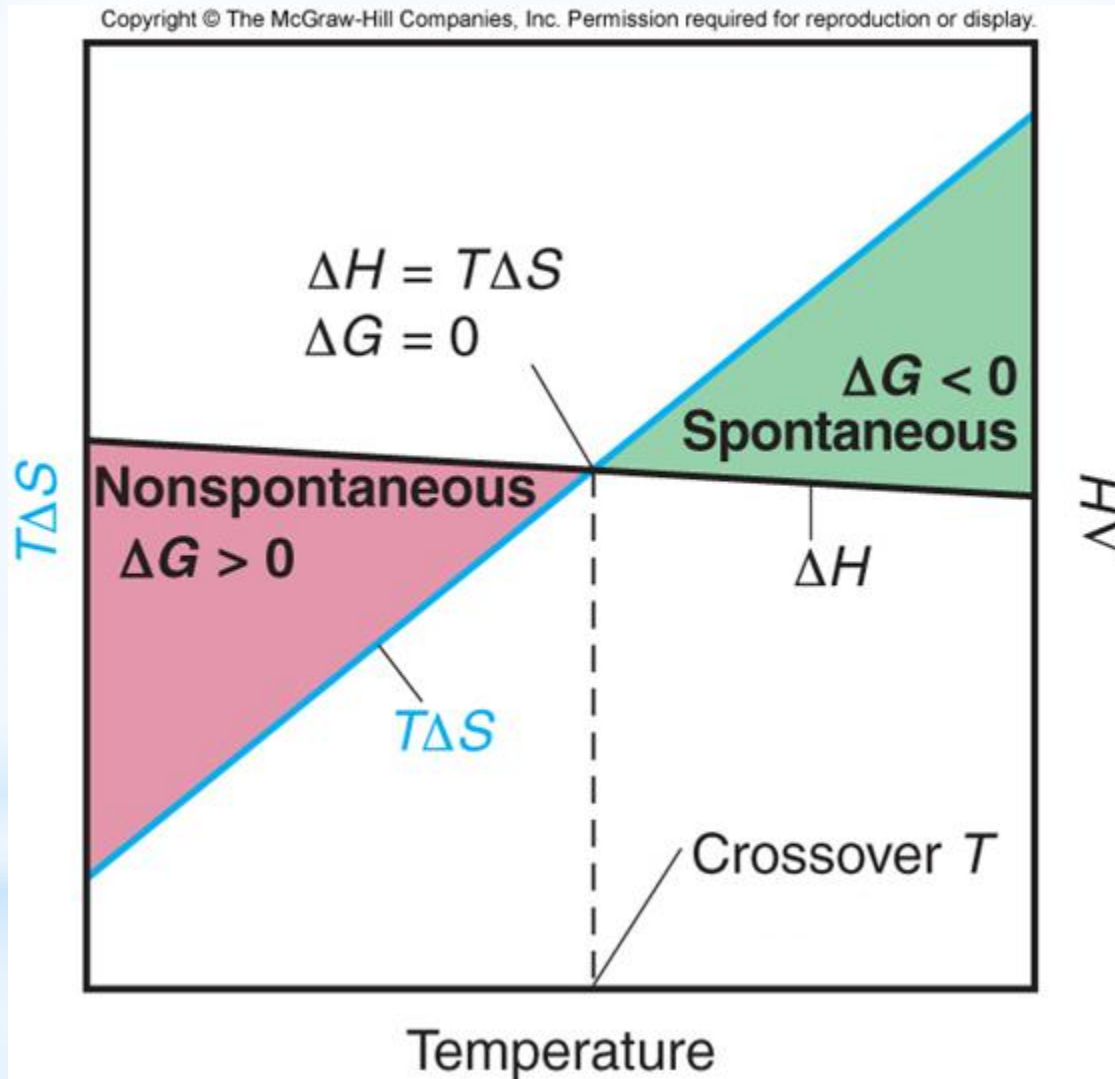
The effect of temperature on spontaneity is most strongly observed when enthalpy and entropy are of the same sign

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

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



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





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  $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$

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

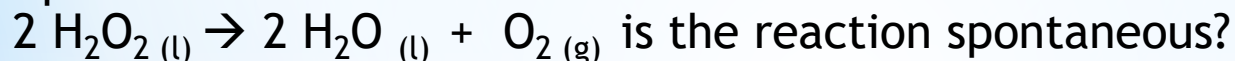
Find out if this reaction is spontaneous at  $25^\circ\text{C}$ , and predict how  $\Delta G$  will change with increasing  $T$  if the enthalpy and entropy changes of the system ( $\Delta C_p$ ) can be considered constant

## Deciding on reaction spontaneity without calculation

The signs of  $\Delta H$ ,  $\Delta S$  and  $\Delta G$  can be used to decide on the spontaneity of reactions as well as the temperature dependence of a reaction

$\Delta H$	$T_K$	$\Delta S$	$\Delta G$	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  $\Delta H$  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

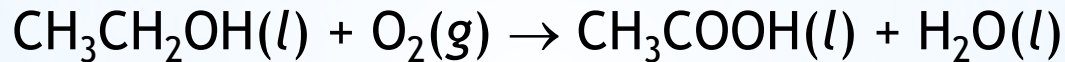
Both lower enthalpy ( $\Delta H$  is negative) and increasing entropy ( $\Delta S$  is positive) favor the forward reaction and the reaction is sure to be spontaneous at all temperatures

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 298 K

The corresponding reaction for the standard Gibbs free energy of formation is the same as that for standard enthalpy of formation,  $\Delta H^\circ$

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

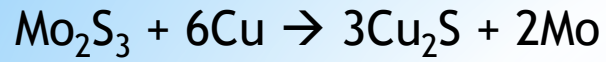
Example - Calculate the change in Gibbs free energy,  $\Delta G^\circ$  for the oxidation of ethyl alcohol to acetic acid using standard free energies of formation



$\Delta G^\circ$ , 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	$\Delta H^\circ_{298}$	$S^\circ_{298}$	a	b	c
Cu(s)	0	33.36	22.6	6.3	
Cu <sub>2</sub> S(s)	-82000	119.59	81.63		
Mo(s)	0	28.59	22.94	5.44	
Mo <sub>2</sub> S <sub>3</sub> (s)	-386650	119.13	126.3	-26.92	