

## 1<sup>st</sup> Law of Thermodynamics

- Used mainly for bookkeeping
- Does...
  1. Indicate energy flow into or out of the system
  2. Indicate how much energy is involved
- Doesn't indicate why the reaction occurs

## Will a reaction be spontaneous?

## Spontaneous Processes

- any process that occurs without outside intervention
  - gas fills a container uniformly, never collects at one end of the container
  - wood burns to form  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and heat, wood doesn't form when  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are heated together
- a spontaneous reaction has a **direction**
- a process spontaneous in one direction...
  - is not spontaneous in the opposite direction

### More Examples:

- egg is dropped and breaks, spontaneous
  - reverse reaction (egg leaps into hand intact) is not spontaneous
- ball rolls down a hill, but never up
- iron rusts if exposed to air and moisture, but rust doesn't change back to iron metal and oxygen

- Direction of a spontaneous reaction can depend on temperature
- Example:
  - ice changes to water spontaneously at  $T > 0^\circ\text{C}$
  - water changes to ice spontaneously at  $T < 0^\circ\text{C}$

## Again, how do you know if a reaction is spontaneous or not?

## And why in one direction and not the other?

**Entropy, S**

- reflects the degree of disorder in a system
  - the larger the S, the more disordered
- processes in which disorder increases tend to be spontaneous
  - Ex: melting, vaporizing, dissolving

- In general, S increases as:
  - solid → liquid → gas
  - number of gas particles increases
  - molar mass increases
  - number of atoms in the chemical formula
  - temperature increases
- associated with **probability**
  - more ways for things to be out of place than for them to be in place

- Ex: Which substance has higher entropy?  
solid CO<sub>2</sub> or gaseous CO<sub>2</sub>
- Ex: Is the entropy increasing or decreasing?  
solid sugar added to water to make a solution  
I<sub>2</sub>(g) condenses on a cold surface to form crystals

**So...  
Is the reaction spontaneous?**

**2<sup>nd</sup> Law of Thermodynamics**

- in any spontaneous process, the entropy of the universe increases.
  - entropy is *not* conserved

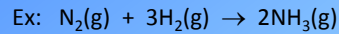
$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$\Delta S_{\text{universe}} > 0$ , spontaneous  
 $\Delta S_{\text{universe}} < 0$ , spontaneous in the opposite direction

**OK...  
How do you know if the  
entropy of the universe  
has increased?**

## Calculating $\Delta S$ for Chemical Reactions

- $\Delta S^\circ_{\text{reaction}} = S^\circ_{\text{prod}} - S^\circ_{\text{react}}$
- $S^\circ$  = standard molar entropy, J/K-mol
- use chart of thermodynamic properties for  $S^\circ$  values



$$\Delta S^\circ = 2(192) - [1(192) + 3(131)]$$

$$= -201\text{J/K}$$

expect negative, because the # gas molecules decreases

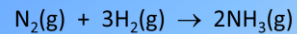
## Calculating $\Delta S$ for the Surroundings

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

- the sign of  $\Delta S_{\text{surr}}$  depends on the direction of heat flow
  - + for exothermic reactions, - for endothermic reactions
- the magnitude of  $\Delta S_{\text{surr}}$  depends on the temperature
  - greater impact at lower temperatures

- Ex: Calculate the  $\Delta S_{\text{surr}}$  at 298K and 1 atm for the following:

(Temperature must be in Kelvin...  $\text{K} = ^\circ\text{C} + 273$ )

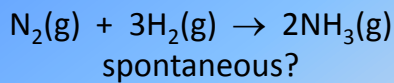


$$S^\circ \text{ for } \text{NH}_3 = -46.19 \text{ kJ/mol}$$

$$\Delta H =$$

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

So...is the reaction



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

**Remember:**  
**Spontaneity of a process is determined by the entropy change it produces in the universe.**

- If  $\Delta S_{\text{system}}$  and  $\Delta S_{\text{surr}}$  are positive, spontaneous
- If  $\Delta S_{\text{system}}$  and  $\Delta S_{\text{surr}}$  are negative, spontaneous in the opposite direction
- If  $\Delta S_{\text{system}}$  and  $\Delta S_{\text{surr}}$  have opposite signs, spontaneity depends on magnitude of each

### Gibbs Free Energy, G

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

- $\Delta G < 0$ , forward reaction spontaneous
- $\Delta G > 0$ , reverse reaction spontaneous
- $\Delta G = 0$ , reaction is at equilibrium
- If  $\Delta H < 0$  and  $\Delta S > 0$  then  $\Delta G < 0$  ..... spontaneous
- If  $\Delta H > 0$  and  $\Delta S < 0$  then  $\Delta G > 0$  ..... not spontaneous

- If  $\Delta H$  and  $\Delta S$  have the same sign,  $\Delta G$  depends on...the magnitude of each and the temperature
- if  $\Delta H$  and  $\Delta S$  are both negative, spontaneous at low temps
- if  $\Delta H$  and  $\Delta S$  are both positive, spontaneous at high temps

- Calculate  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  for the following reaction:  
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$  at  $25^\circ\text{C}$  1 atm

Given:	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/K mol)
$\text{SO}_2(\text{g})$	-297	248
$\text{SO}_3(\text{g})$	-396	257
$\text{O}_2(\text{g})$	0	205

$\Delta H^\circ =$

$\Delta S^\circ =$

$\Delta G^\circ =$

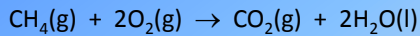
(verify with  $\Delta G_f^\circ$ , pg 1019: products – reactants = -140 kJ)

### Another way to determine G...

$$\Delta G^\circ_{\text{rxn}} = \Delta G^\circ_{\text{f prod}} - \Delta G^\circ_{\text{f react}}$$

( $\Delta G^\circ_{\text{f}} = 0$  for elements)

Ex: Calculate Gibbs Free Energy:



-50.8    0            -394.4    -237

Spontaneous?

Ex: At what temperature is the following process spontaneous?  $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$

(i.e. What is the boiling point of bromine?)

$$\Delta H = 31.0 \text{ kJ/mol} \quad \Delta S = 93.0 \text{ J/K mol}$$

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

$$T = \frac{\Delta H}{\Delta S} = \frac{31000 \text{ J/mol}}{93.0 \frac{\text{J}}{\text{K mol}}} = 333 \text{ K}$$

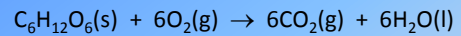
Above 333 K,  $T\Delta S > \Delta H$ , and  $\Delta G$  is negative

Above 333 K, this reaction (vaporization) is spont.

## Coupled Reactions

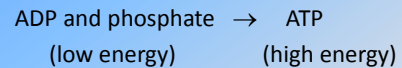
- Using one spontaneous reaction to drive another non-spontaneous reaction
- Common in biological systems

- Ex: Metabolism of foods releases energy:



$$\Delta G^\circ = -2880 \text{ kJ}$$

- This free energy is used to convert:



- When  $\text{ATP} \rightarrow \text{ADP}$ , the energy released is used to drive other reactions

Whether or not a reaction is ***spontaneous*** says nothing about how ***fast*** a reaction will occur.

We need both ***thermodynamics*** and ***kinetics*** to describe a reaction fully.