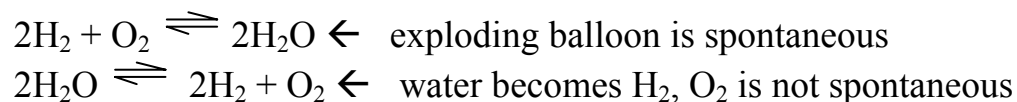


## LECTURE 20. THERMODYNAMIC OVERVIEW—A QUALITATIVE APPROACH

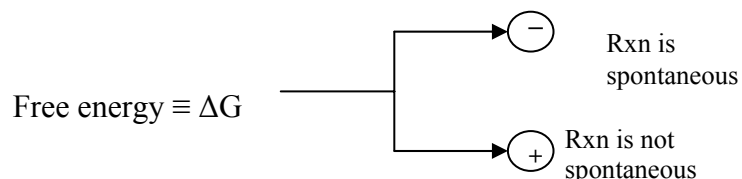
Today's lecture is a general overview of thermodynamics from a qualitative perspective. To really be able to understand thermo, you need to look at a chemical reaction and talk about it in the context of relative changes in state functions. The lecture actually parallels a hand you can download called, "Thoughts on Thermodynamics." If you can actually learn what is on this handout, and be able to explain it unassisted to a classmate, you will do well.

### How to Know if a Reaction Happens

First, one of the important consequences of thermodynamics is the ability to explain whether a reaction occurs or not. Note that for every spontaneous reaction, there is a reverse non-spontaneous reaction and it would be nice to look at a reaction and tell whether it is going to happen as written or as the reverse. For example:



The state function that determines spontaneity is free energy,  $\Delta G$ :



So when you look at a reaction, if you know it occurs from experience, you know it has  $\equiv \Delta G = \ominus$ .

**Example.** Consider  $\text{AgNO}_3 + \text{NaCl} \rightarrow \text{AgCl} + \text{Na}^+ + \text{NO}_3^-$

You know from solubility rules that  $\text{AgCl}$  is insoluble and the reaction shifts to the right, so you know that for this reaction,  $\Delta G$  is  $\ominus$

## Signs and thermo—Be the System

So what is the source of this idea about thermodynamic signs? Why was  $\Delta G = \ominus$  for a spontaneous reaction defined as spontaneous. Is it arbitrary? NO.

### How sign convention happens: “Be the System”

Sign convention views the assignment of (+) and (-) for thermo processes on the basis of whether the system gains or loses

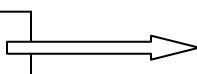
**If the system gains, the sign is (+)**

**If the system loses, the sign is (-)**

**Heat Absorbed**  
(+) Endothermic  
Bonds Formed

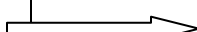
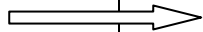


**System**

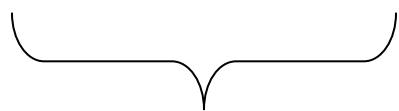


**Heat Leaves**  
(-) Exothermic  
Bonds Break

(+) **Work Done**  
**On System.** Bomb is  
Loaded



(-) **Work Done**  
**on Surrounding**  
Bomb Explodes



Good for System Strength



Bad for System Strength

This “**Be the System**” idea can be hard because we are the surroundings and like to think we are what matters. But in thermo, it is the system.

**Example:** A Fire Burns Down a House—Is the process exothermic or endothermic. Is work done on this system or the surroundings?



**Exothermic:** (-), heat evolves, the wood of the house gets cold, i.e. the strong wood bonds become weak bonds  $\text{CO}_2 + \text{H}_2\text{O}$  bonds.

**Work Done on the Surroundings:** (-), gas evolves, wood becomes  $\text{CO}_2 + \text{H}_2\text{O}$ . A bomb is formed as the volume of the house expands.

## More thoughts on work and signs

**Note:**  $w = -P\Delta V = -\Delta nRT$

Why is the negative sign? Note that in a reaction with work done on the system



But since we know we must be (+), (work is being added to the system), then the minus sign is needed to correct sign.

$w = -\Delta nRT = -(-)RT = (+)RT$

Understanding signs is vital, because every thermo answer has a sign, and you can do the math and get the right number, but choose the wrong sign and get the entire problem wrong.

## Temperature dependence of free energy

As we will learn, there are two quantities that can be measured to determine free energy in the equation in a temperature dependent reaction, enthalpy,  $\Delta H$ , and entropy,  $\Delta S$ :

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

Case 1: (Always spontaneous)

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

$\ominus$  if  $\ominus$  and  $\oplus$

Conditions for  
 $\Delta G$  always  
spontaneous

(Note T is always + so a  
positive  $\Delta S$  makes  $-T \Delta S$

Case 2: (Never spontaneous)

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

$\oplus$  if  $\oplus$  and  $\ominus$

Conditions for  $\Delta G$   
always non-  
spontaneous

Case 3: (Temperature dependent)

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

⊖ if ⊕ and ⊕ and T large

⊖ if ⊖ and ⊖ and T small

**Example of temperature dependent spontaneity:**

Ice melting:  $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$

Is it spontaneous? It is at high T, but not as in a freezer. So it must be the high T spontaneous case.

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

← at high T,  
-TΔS overcomes ΔH +

**On to explain Energy in 3 forms:**

ΔH

enthalpy state function  
describing heat of  
reaction

T ΔS

entropy state function  
describing disorder of  
reaction

W

work not a state function.  
Describes Fxd done by  
gas molecules

**First Enthalpy, ΔH**

ΔH ≡ enthalpy can be ⊕ or ⊖

⊖ ≡ heat given off to surroundings ≡ **exothermic**

**Example:**  $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{OH})_2 + \text{heat}$  Cooks an egg, makes a mess and ΔH is ⊖

$\oplus$   $\equiv$  heat absorbed so surroundings cold  $\equiv$  **endothermic**

Example:  $\text{Ba}(\text{OH})_2 + \text{NH}_4\text{NO}_3 \rightarrow \text{NH}_3$  and other stuff + cold and  $\Delta H$  is  $\oplus$

In general, combustion reactions are exothermic and most spontaneous reactions are exothermic. But not all (see last example above).

•• So we can say, exothermicity promotes spontaneity, but is not a necessary condition for spontaneity.

There are 3 ways you will be asked to determine  $\Delta H$

- Calorimetry  $mC(\Delta T)$  calculation
- Heat of formation calculation
- Bond energy calculation

### **Entropy: tendency to disorder. In a chemical system $\Delta S$ :**

$\oplus$   $\equiv$  entropy increases

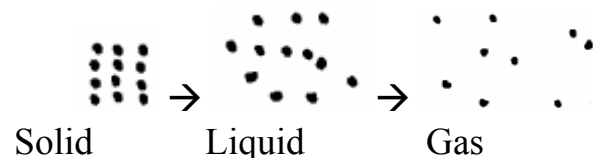
$\ominus$   $\equiv$  entropy decreases

As you see from  $\Delta G = \Delta H - T\Delta S$ , you want  $\Delta S$  positive for spontaneity. And this makes sense, reactions happen because something is made easier, and increasing disorder, like creating a messy room, is easier than creating order (cleaning up a room).

So can we predict the sign of  $\Delta S$ ?

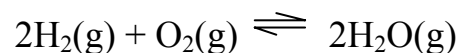
Yes, using common sense.

1. Increased temperature increases  $\Delta S$ . Why? When it gets hotter, kinetic energy goes up, velocity goes up, molecules separate more.
2. Increased volume increases  $\Delta S$ . Why? If molecules that bounced around in a cup will be more disordered bouncing around in a gallon jug.
3. Solid  $\rightarrow$  liquid  $\rightarrow$  gas increases  $\Delta S$ . Why?



4. Increased  $\Delta n$  of reaction increases  $\Delta S$ . Why? More molecules, more mess.

So we can look at a chemical reaction and predict  $\Delta S$ :



$\Delta S$  is  $\ominus$ . Why?

Two reasons.

first  $\Delta n = -1$  ( $3 \rightarrow 2$ ) so fewer particles made

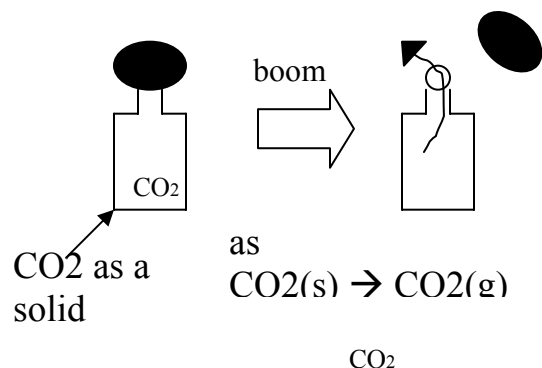
and

second,  $\text{g} \rightarrow \text{s}$  so the matter is more ordered.

## Work

**On to work,  $w$ ,** which is the ability of a chemical reaction to push objects around, as in  $Fx = w$ . If you think about it, gas molecules under pressure will exert a force as they achieve large volume.

$$w = -P\Delta V$$



This is actually what makes a bomb.

1. enclosed container
2. increase in gas pressure

Note we only talk about gases because solids  $\rightarrow$  liquids don't change volume very much.

So can we calculate  $w$ ? From the ideal gas law:

$$W = -P\Delta V = -\Delta nRT \text{ (gas law)} \quad \text{and for } R = 8.3 \text{ J/mole K at } 300 \text{ K} \quad \text{so} \quad RT \approx 2.5 \text{ kJ (at room temperature)}$$

So all we need to do is find  $\Delta n_{\text{gas}}$  and, at room temperature, work for a gas is a multiple of 2.5 kJ/mole

**Example:**  $2\text{H}_2\text{O}(\text{g}) \rightleftharpoons 2\text{H}_2 + \text{O}_2$        $\Delta n_{\text{gas}} = 3 - 2 = +2 \Rightarrow w = -\Delta nRT = -1(8.3)(300) = -2.5 \text{ kJ}$

**Example:**  $2\text{H}_2\text{O}(\text{l}) \rightleftharpoons 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$        $\Delta n_{\text{gas}} = 3 - 0 = 3 \Rightarrow w = -\Delta nRT = -(3)(8.3)(300) = -7.5 \text{ kJ}$

See how easy a work,  $w$ , calculation is?



