

## Thermodynamics

AP Chemistry 30L – Ms. Hayduk

### Internal Energy and Heat Flow

- Internal energy is all energy in a chemical system
- Heat flow changes energy of system
- Increased internal energy may cause:
  - Temperature increase (kinetic)
  - Phase change
  - Chemical reaction
- Decrease can cause first two, not reaction

### Calculating Heat

- Calorimetry: process of measuring heat through temperature change of a system
- Measured by:
 
$$q = mc\Delta T$$
  - Where q is quantity of heat (J), m is mass of substance (g), c is specific heat capacity of substance (J/g°C) and  $\Delta T$  is temperature change
- $q = -\Delta H$  at constant pressure

## Laws of Thermodynamics

### Zeroth Law

- Heat flows from hot to cold

### First Law

- Energy and matter are conserved

### Second Law

- Matter tends toward chaos

### Third Law

- Entropy (disorder) of a pure crystal at 0K is 0

### Heat and Work

- Energy exchanged is accounted for with heat (q) and work (w)
 
$$\Delta E = q + w$$
- Work = force acting on an object
  - In chemistry, done BY a gas through expansion or TO a gas by compression
  - Pressure/volume work:  $w = -P\Delta V$

### Ways to Calculate Enthalpy

1. Calorimetry
  - Experimental
  - $q = mc\Delta T$
2. Enthalpy of Formation
  - From table of standard values
  - Production of one mole of a compound from elements in standard states, 0 for elements
  - $\Delta H^\circ_{rxn} = \sum H^\circ_f(\text{products}) - \sum H^\circ_f(\text{reactants})$

## Ways to Calculate Enthalpy

### 3. Hess' Law

- Sum of enthalpies of chemical equations that add to overall equation to get overall enthalpy
- Enthalpy is a state function – not path dependent

### 4. Stoichiometry

- Use  $\Delta H$  for a balanced reaction (kJ/mol)
- e.g. if 1.00 g of Fe reacts, how much heat is released if:  

$$4 \text{ Fe} + 3 \text{ O}_2 \rightarrow 2 \text{ Fe}_2\text{O}_3 \quad \Delta H = -1652 \text{ kJ/mol}_{\text{rxn}}$$

## Ways to Calculate Enthalpy

### 5. Bond Energy

- $\Delta H^\circ_{\text{rxn}} = \Sigma BE_{\text{broken}} - \Sigma BE_{\text{formed}}$
- Use Lewis structures and a table of values for bond energies

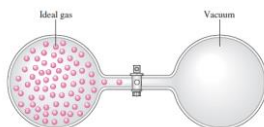
## Entropy

- Disorder of a system
- Entropy for a substance is specific at a certain temperature, relative to the substance at 0 K, where  $S = 0$
- Less disorder ( $-\Delta S$ ) or more disorder ( $+\Delta S$ )

## Second Law

- Why do systems tend towards disorder?
- Based on probability – there are many more ways for a system to be disordered than ordered

### Example: Second Law



### Physical Evidence of Entropy

- Greater disorder/randomness = larger  $S$
- Increases from solid to liquid to gas
- Increases when pure solid or liquid dissolves in water (EXCEPT carbonates)
- Volume is increased in a gaseous system
- More complex molecules or more molecules are formed

## Example: Predicting Entropy

Predict the sign of  $\Delta S$  for each of the following processes:

- Solid sugar is added to water to form a solution
- Iodine vapour condenses on a cold surface to form crystals

## Calculating Entropy

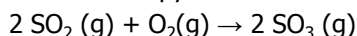
- Hess' Law
- Table of Standard Values

$$\Delta S^\circ_{rxn} = \Sigma \Delta S^\circ_{products} - \Sigma \Delta S^\circ_{reactants}$$

Note that entropy is given in **J/K·mol**, not kJ!

## Example: Entropy Calculation

Determine the entropy for the reaction:



Substance	S° (J/K·mol)
SO <sub>2</sub> (g)	248.1
O <sub>2</sub> (g)	205.3
SO <sub>3</sub> (g)	256.6

## Entropy for Phase Changes

- For reversible phase changes (constant temperature) or systems at equilibrium:

$$\Delta S = \frac{-\Delta H}{T}$$

## Spontaneity of Reactions

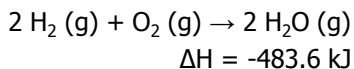
- Terms to know:
  - Enthalpy,  $\Delta H$  (heat content of a system)
  - Entropy,  $\Delta S$  (disorder of a system)
- Spontaneous means a reaction will occur without outside intervention, either quickly or slowly

## Spontaneity of Reactions

- Exothermic reactions are generally favoured ( $+\Delta H$ )
- More disorder is generally favoured ( $+\Delta S$ )
- May be determined by looking at  $\Delta S_{univ}$ 

$$\Delta S_{system} + \Delta S_{surroundings} = \Delta S_{universe}$$
- If  $\Delta S_{univ}$  is +, reaction is spontaneous
- If  $\Delta S_{univ}$  is -, reaction is non-spontaneous

## Example: Spontaneity



- Determine  $\Delta S_{\text{system}}$  using standard entropies.
- Determine  $\Delta S_{\text{surroundings}}$  using enthalpy. (Remember that  $\Delta H_{\text{rxn}} = -\Delta H_{\text{surroundings}}$ )
- Determine  $\Delta S_{\text{universe}}$ . Is this reaction spontaneous?

## Gibb's Free Energy

- Determines if reaction is thermodynamically favoured (spontaneous) or not
- Negative is spontaneous
 
$$\Delta G^{\circ}_{\text{rxn}} = \Sigma \Delta G^{\circ}_{\text{products}} - \Sigma \Delta G^{\circ}_{\text{reactants}}$$
 to calculate from a table of values  
 Or, use Hess' law

## Example: Gibb's Free Energy

Find the free energy of formation for the oxidation of water to produce hydrogen peroxide.

V.I.E.

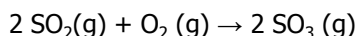
$$\Delta G = \Delta H - T\Delta S$$

Calculate enthalpy and entropy from a table of values.

	$\Delta G^{\circ}_f$
H <sub>2</sub> O (l)	-56.7 kcal/mol
O <sub>2</sub> (g)	0 kcal/mol
H <sub>2</sub> O <sub>2</sub> (l)	-27.2 kcal/mol

## Example: Very Important Equation

Determine  $\Delta G$  for the following reaction at 25°C and 1 atm:



Substance	$\Delta H^{\circ}_f$ (kJ/mol)	$S^{\circ}$ (J/K · mol)
SO <sub>2</sub> (g)	-297	248
SO <sub>3</sub> (g)	-396	257
O <sub>2</sub> (g)	0	205

## Free Energy for an Equilibrium System

- If the system is not at equilibrium:

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

R is universal gas constant, 8.314 J/mol·K  
 T is temperature in Kelvin  
 Q is reaction quotient

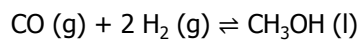
- At equilibrium:

$$\Delta G = RT \ln K$$

R is universal gas constant, 8.314 J/mol·K  
 T is temperature in Kelvin  
 K is equilibrium constant

### Example 1: Equilibrium

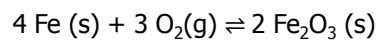
To synthesize methanol:



Calculate  $\Delta G$  at 25°C for this reaction where carbon dioxide is 5.0 atm and hydrogen is 3.0 atm.

### Example 2: Equilibrium

When iron rusts:



Calculate the equilibrium constant for this reaction at 25°C.

Substance	$\Delta H_f^\circ$ (kJ/mol)	$S^\circ$ (J/K · mol)
Fe <sub>2</sub> O <sub>3</sub> (s)	-826	90
Fe(s)	0	27
O <sub>2</sub> (g)	0	205