

AP Chemistry Unit 5 - Thermodynamics

Thermochemistry - the study of heat (=energy) in chemistry

Thermodynamics - the study of heat (energy) as it changes

Kinetic Energy - energy of motion

- $E_k = \frac{1}{2} mv^2$
 - E = Energy in Joules (J)
 - m = mass (kg)
 - v = velocity (m/s)

Universe = system + surroundings

- system - confined to only what is being studied
- surroundings - everything else

Internal Energy

- includes all of the potential and kinetic energy of all the parts of the system
- $\Delta E = E_f - E_i$ (change in internal energy)
- $+\Delta E$ = the system has gained energy (surroundings lose)
- $-\Delta E$ = the system has lost energy (surroundings gain)
- $\Delta E = q + w$
 - q = heat (J)
 - w = work (J)
- $+q$ = heat added to system
- $-q$ = heat lost by system
- $+w$ = work done on system by surroundings
- $-w$ = work done by system on surroundings

endothermic (heat in) - system gains energy, $+\Delta E$

- surroundings lose energy so container often feels cold

exothermic (heat out) - system loses energy, $-\Delta E$

- surroundings gain energy so container will feel warm

State function

- a property of a system that is determined only by its present state
- does not depend on the pathway it took to reach that state
- Common state functions:
 - pressure, temperature, volume, internal energy, entropy

Enthalpy (H)

- heat flow
- $\Delta H = \Delta E + P\Delta V$ (at constant pressure)
 - H = enthalpy (J)
 - E = internal energy (J)
 - PV = work done by changing pressure, volume (J)
- $+\Delta H$ = system has gained heat
- $-\Delta H$ = system has lost heat

Determine the sign of ΔH

- ice cube melting
 - $+\Delta H$ (water gains energy to change from solid to liquid)
- 1 g of butane (C_4H_{10}) undergoes complete combustion
 - ΔH (heat is released)
- What if the system is contained so no heat can be released? Will a piston rise or fall?
 - $2 C_4H_{10} + 13 O_2 \rightarrow 8 CO_2 + 10 H_2O$
 - volume of products > volume of reactants
 - piston will rise to maintain a constant pressure

Enthalpy of Reactions

$$\Delta H = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

- enthalpy is an extensive property (depends on amount)
- enthalpy change for a reverse reaction will be the same in magnitude, opposite in sign
- enthalpy change depends on state of reactants and products

How much heat is released when 4.5 g of methane gas is burned in a constant pressure system? ($\Delta H_{\text{rxn}} = -890 \text{ kJ}$) (-250 kJ)

Calorimetry

-measurement of heat flow

- heat capacity - the amount of heat required to raise the temperature of an object by 1K
- molar heat capacity - the amount of heat required to raise 1 mole of a substance by 1K
- specific heat - the amount of heat required to raise 1 g of a substance by 1 K

$$s = \frac{q}{m\Delta T}$$

- s = specific heat (J/gK)
- q = amount of heat exchange (J)
- m = mass (g)
- ΔT = temperature change (K)

Constant Pressure Calorimetry

How much heat is needed to warm 250 g of water from 22 °C to 98 °C? The specific heat of water is 4.18 J/g K. (7.9×10^4 J)

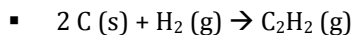
What is the molar heat capacity of water? ($C = 75.2$ J/mol K)

A student mixes 50 mL of 1.0 M HCl and 50 mL of 1.0 M NaOH in a calorimeter and notices that the temperature rises from 21.0 °C to 27.5 °C. Calculate the enthalpy change if the total volume is 100 mL, the density is 1.0 g/mL, and the specific heat is 4.18 J/gK. (-2.7 kJ)

Hess's Law

- if a reaction is carried out in a series of steps, the ΔH for the overall reaction will equal the sum of the enthalpy changes for the individual steps.

Calculate ΔH for



- Given
 - $\text{C}_2\text{H}_2 \text{ (g)} + \frac{5}{2} \text{ O}_2 \text{ (g)} \rightarrow 2 \text{ CO}_2 \text{ (g)} + \text{ H}_2\text{O (l)} \quad \Delta H = -1299.6 \text{ kJ}$
 - $\text{C (s)} + \text{ O}_2 \text{ (g)} \rightarrow \text{ CO}_2 \text{ (g)} \quad \Delta H = -393.5 \text{ kJ}$
 - $\text{H}_2 \text{ (g)} + \frac{1}{2} \text{ O}_2 \text{ (g)} \rightarrow \text{ H}_2\text{O (l)} \quad \Delta H = -285.8 \text{ kJ}$

($\Delta H_{\text{rxn}} = 226.8 \text{ kJ}$)

Enthalpy of Formation ΔH_f

- the amount of energy needed to form a 1 mole of a compound from its elements at standard conditions
- Note: Standard conditions here are 1 atm at 298 K
 - (vs. 1atm, 0°C for molar volume of a gas)

What is the ΔH_f for argon?

- 0! There is no formation of a compound.

Which reactions are formations?

- $2 \text{ Na (s)} + \frac{1}{2} \text{ O}_2 \text{ (g)} \rightarrow \text{Na}_2\text{O (s)}$
 - yes
- $2 \text{ K (l)} + \text{Cl}_2 \text{ (g)} \rightarrow 2 \text{ KCl (s)}$
 - no, K would be a solid under standard conditions
 - two moles of product are formed
 - $\text{K (s)} + \frac{1}{2} \text{ Cl}_2 \text{ (g)} \rightarrow \text{KCl (s)}$
- $\text{C}_6\text{H}_{12}\text{O}_6 \text{ (s)} \rightarrow 6 \text{ C (diamond)} + 6 \text{ H}_2 \text{ (g)} + 3 \text{ O}_2 \text{ (g)}$
 - No, decomposition
 - $6 \text{ C (graphite)} + 6 \text{ H}_2 \text{ (g)} + 3 \text{ O}_2 \text{ (g)} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 \text{ (s)}$
- $\Delta H_{\text{rxn}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$

Calculate the enthalpy of reaction for the combustion of 1 mole of methanol (CH_3OH , -1367 kJ)

Strength of Covalent Bonds

- Bond enthalpy – ΔH for the breaking of a bond in one mole of a gaseous substance
 - Always positive
 - As ΔH increases, bond strength increases
 - Generally, as the number of bonds between two atoms increases, strength increases and the bond length decreases

$$\Delta H_{\text{rxn}} = \Sigma (\Delta H_{\text{bonds broken}}) - \Sigma (\Delta H_{\text{bonds formed}})$$

Estimate the enthalpy of reaction for the combustion of ethane (C_2H_6) gas. ($\Delta H_{\text{rxn}} = -1416 \text{ kJ}$)

TABLE 8.4 Average Bond Enthalpies (kJ/mol)

Single Bonds							
C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						
Multiple Bonds							
C=C	614	N=N	418	O ₂	495		
C≡C	839	N≡N	941				
C=N	615	N=O	607	S=O	523		
C≡N	891			S=S	418		
C=O	799						
C≡O	1072						

First Law of Thermodynamics

- Energy cannot be created or destroyed.

Spontaneous process

- One that proceeds on its own without outside assistance
- The reverse reaction will be non-spontaneous

Predict which are spontaneous...

- *When a piece of metal at 150 °C is added to water at 40 °C, the water gets hotter.*
 - Spontaneous
- *Water at room temperature decomposes into H₂ and O₂ gas.*
 - Not spontaneous; reverse is spontaneous once ignited by a spark or flame
- *Benzene (C₆H₆) vapor at 1 atm condenses to become a liquid at the normal boiling point.*
 - Process is at equilibrium – neither forward or reverse reaction is spontaneous

Entropy

- S (J/K) – the extent of randomness in a system

Mercury is a silvery liquid at room temperature. The normal freezing point is -38.9 °C, and its ΔH_{fus} is 2.29 kJ/mol. What is the entropy change when 50.0 g of liquid mercury freezes at the normal freezing point? (-2.44 J/K (negative entropies tend to be non-spontaneous))

Second Law of Thermodynamics

- Any irreversible process results in an overall increase in entropy, where as a reversible process results in no change in entropy.
 - i.e. The entropy of the universe is always increasing
- Entropy increases for ...
 - Gases formed from liquids or solids
 - Liquids or solutions formed from solids
 - Reactions where there are more product gas molecules than reactant molecules

Is ΔS + or -?

- $\text{H}_2\text{O (l)} \rightarrow \text{H}_2\text{O (g)}$
 - positive
- $\text{Ag}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)} \rightarrow \text{AgCl (s)}$
 - negative
- $4 \text{ Fe (s)} + 3 \text{ O}_2 \text{ (g)} \rightarrow 2 \text{ Fe}_2\text{O}_3 \text{ (s)}$
 - negative
- $\text{N}_2 \text{ (g)} + \text{O}_2 \text{ (g)} \rightarrow 2 \text{ NO (g)}$
 - Need more information

Third Law of Thermodynamics

- The entropy of a pure crystalline solid at 0K is 0.

Entropy Changes in Reactions

- $\Delta S^\circ = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$

Using Appendix C, calculate the change in entropy for the formation of ammonia gas from hydrogen and nitrogen gas. (-198.3 J/K)

Gibbs Free Energy

- Determines the spontaneity of a reaction
- Exothermic reactions and those that increase in entropy tend to be spontaneous, but they could be competing factors (endothermic, increase in entropy)
- $\Delta G = \Delta H - T\Delta S$
 - $\Delta G < 0$, reaction is spontaneous
 - $\Delta G > 0$, reaction is not spontaneous (reverse rxn will occur)
 - $\Delta G = 0$, reaction is at equilibrium (btw. reactants & products)

Effect of Temperature on Spontaneity of Reactions

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics
-	+	-	-	Spontaneous at all temperatures
+	-	+	+	Non-spontaneous at all temperatures
-	-	+	+ or -	Spontaneous only at low T
+	+	-	+ or -	Spontaneous only at high T

Using Appendix C, determine whether or not the reaction of forming ammonia gas from nitrogen and hydrogen gas is spontaneous at 25 °C and at 500 °. (-33.3 kJ, 61 kJ)