Lecture Presentation

Chapter 9
Thermochemistry:
Chemical Energy

9.1, 9.2, 9.3, 9.4, 9.5, 9.6,
9.7, 9.9, 9.10, 9.11, 9.12,
9.13, 9.14, 9.16, 9.18, 9.19,
9.20, 9.21, 9.23, 9.24, 9.26,
9.29, 9.30, 9.34, 9.42, 9.46,
9.62, 9.66, 9.68, 9.76, 9.80,
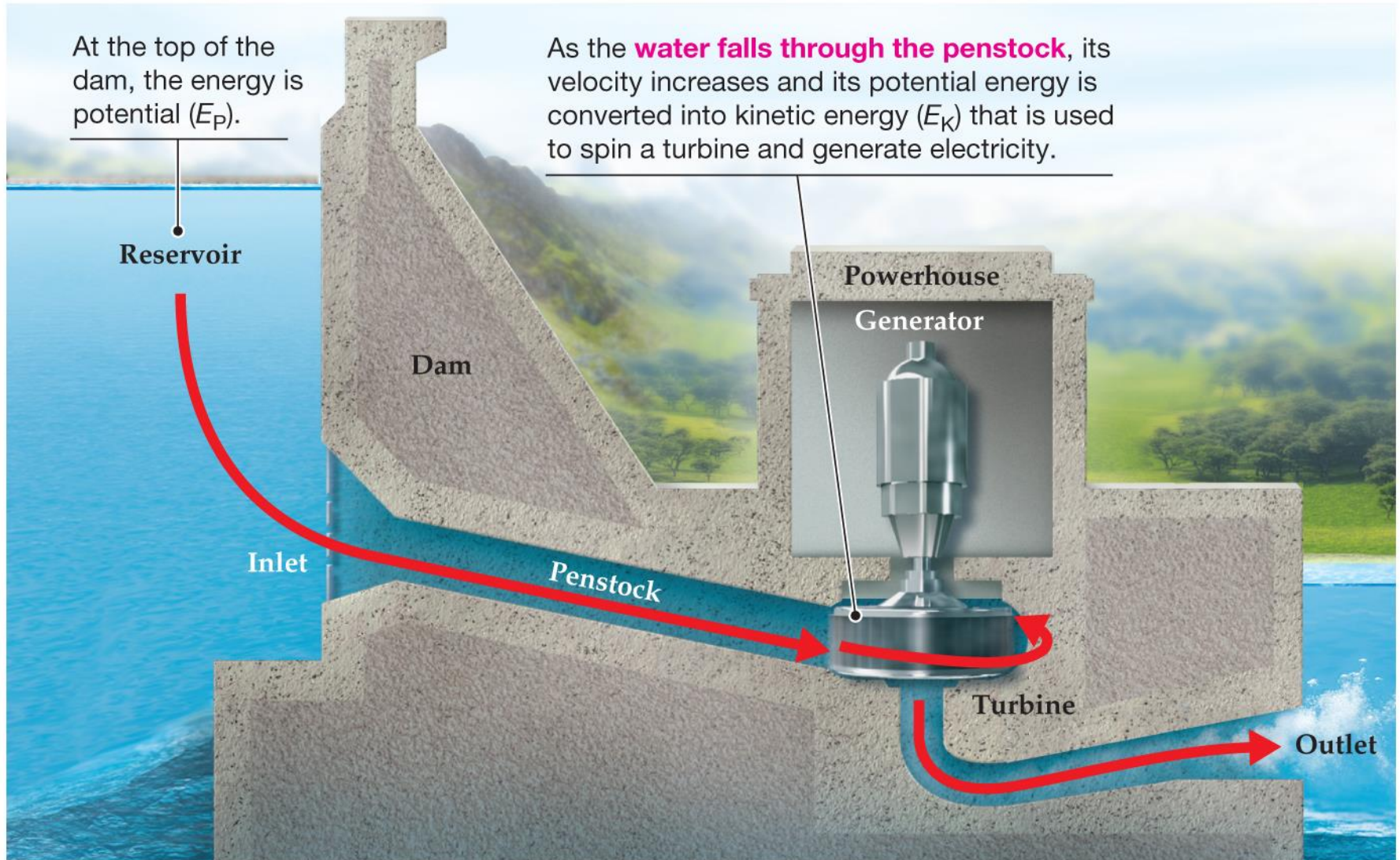9.86, 9.90, 9.94, 9.102,
9.106, 9.122

Seventh Edition

CHEMISTRY

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Energy and Its Conservation

Conservation of Energy Law: Energy cannot be created or destroyed; it can only be converted from one form to another. (another way to state - First Law of Thermodynamics)

First Law of Thermodynamics: The total internal energy (E) of an isolated system is constant. (energy of the universe is constant)

Energy and Its Conservation

At the top of the dam, the energy is potential (E_P).

As the **water falls through the penstock**, its velocity increases and its potential energy is converted into kinetic energy (E_K) that is used to spin a turbine and generate electricity.

Reservoir

Dam

Powerhouse

Generator

Inlet

Penstock

Turbine

Outlet

potential energy → kinetic energy → electricity

Energy and Its Conservation

Thermal Energy: The kinetic energy of molecular motion. It is measured by finding the *temperature* of an object.

Heat: The amount of thermal energy transferred from one object to another as the result of a *temperature difference* between the two
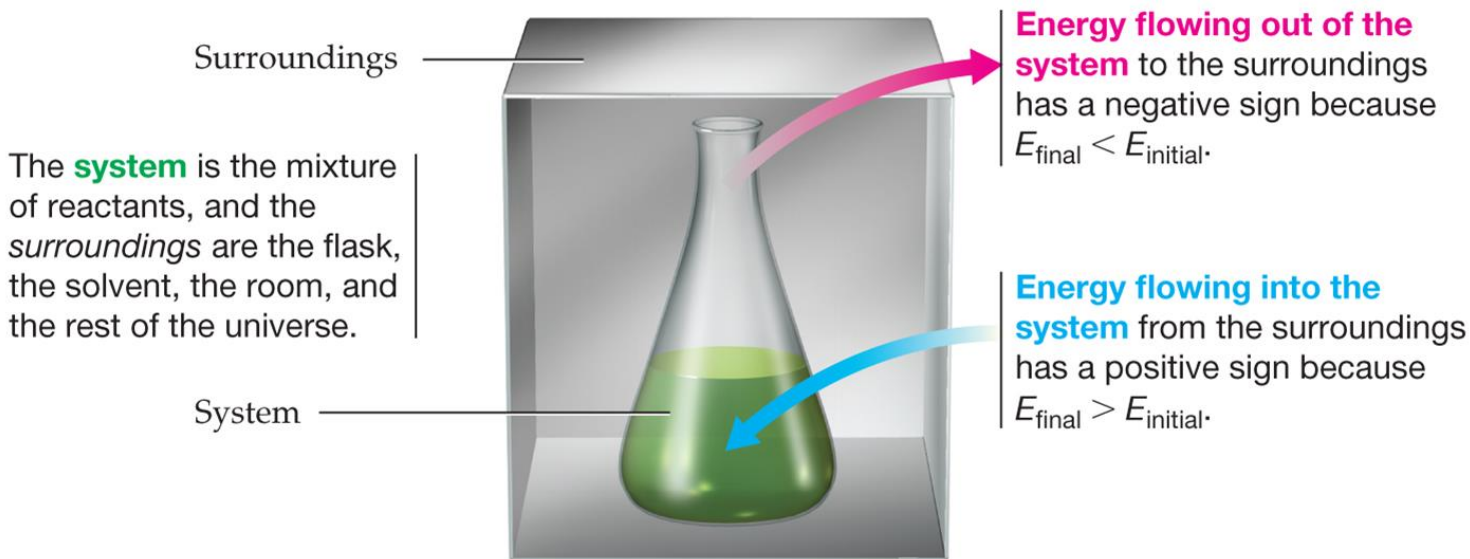
Internal Energy and State Functions

First Law of Thermodynamics: The total internal energy E of an isolated system is constant. (but in reality system is NOT isolated so measure change in internal energy of the system) (energy of the universe is constant)

$$\Delta E = E_{final} - E_{initial}$$ system

The energy change is the difference between final and initial states.

$$\Delta E = E_{final} - E_{initial}$$

Surroundings

Energy flowing out of the system to the surroundings has a negative sign because $E_{final} < E_{initial}$.

The **system** is the mixture of reactants, and the *surroundings* are the flask, the solvent, the room, and the rest of the universe.

System

Energy flowing into the system from the surroundings has a positive sign because $E_{final} > E_{initial}$.

Energy as a State Function

- **State function** (**state property**): Property that does not depend in any way on the system's past or future (independent of the pathway taken between the two states)

Parts of the Universe

- **System**: Part of the universe on which one wishes to focus attention
  - Example - System can be defined as the reactants and products of a reaction
- **Surroundings**: Includes everything else in the universe
  - Example - Surroundings consist of anything else other than the reactants and products

Types of Reactions

- **Exothermic**: Reaction that releases heat to surrounding [reaction (system) releases heat]
  - Heat flows out of the system (hold reaction beaker, hand feels hot) (ΔE = negative)
  - Example - Combustion of methane

- **Endothermic**: Reaction that absorbs heat from the surroundings (add heat to reaction)
  - -- Heat flows into system (hold reaction beaker, hand feels cold) (ΔE = positive)
  - Example - Formation of nitric oxide

Internal Energy and State Functions
(view everything from the point of view of system)

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \text{802 kJ energy}$$
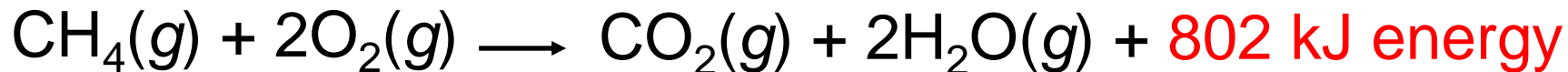
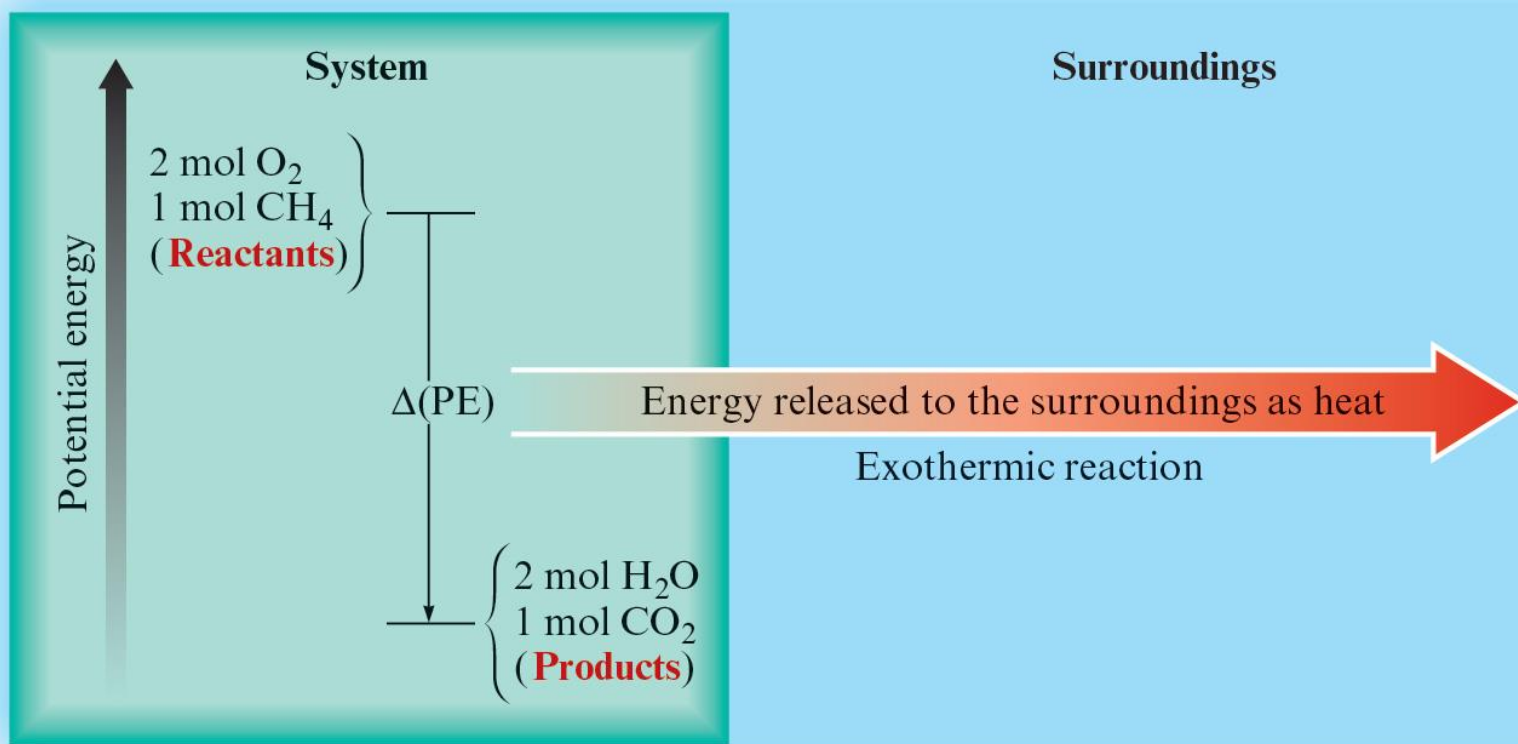$$\Delta E = E_{final} - E_{initial} = -802 \text{ kJ (system)}$$

802 kJ is released when 1 mol of methane, CH_4, reacts with 2 mol of oxygen to produce 1 mol of carbon dioxide and 2 mol of water.   (system is reaction)

Product has 802 kJ less energy than reactant.

System has lost energy to surroundings.

Exothermic reaction

Energy Diagram for the Combustion of Methane, an Exothermic Process

Energy and Enthalpy - system exchanges energy with surrounding by either exchanging heat or doing work

$$\Delta E = q + w = \text{heat + work}$$

q = heat transferred
+ *system gains heat*

w = work = $-P\Delta V$

$$q = \Delta E + P\Delta V$$

Constant Volume ($\Delta V = 0$): $q_v = \Delta E$

Constant Pressure: $q_p = \Delta E + P\Delta V$

$q_p = (\Delta H) = \text{enthalpy}$

Internal Energy and Enthalpy

$$\Delta E + P\Delta V = \Delta H$$

work

Constant V

Constant P

Enthalpy change
or
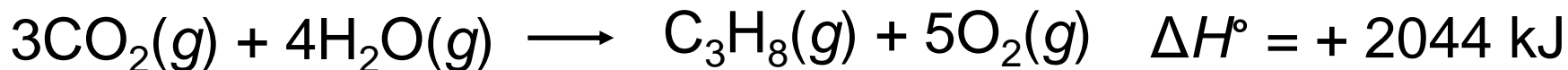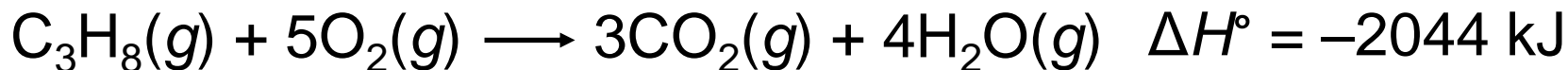**Heat of reaction (at constant pressure)**

Enthalpy is a state function whose value depends only on the current state of the system, not on the path taken to arrive at that state.

$$\Delta H = H_{final} - H_{initial}$$

$$= H_{products} - H_{reactants}$$

PΔV is usually small so   **$\Delta E = \Delta H$ is a good approximation**
Although as in the example on page 320 in text, get most of work from a car combustion from PΔV work

Thermochemical Equations and the Thermodynamic Standard State

Thermodynamic Standard State: Most stable form of a substance at 1 atm pressure and at a specified temperature, usually 25 °C; 1 M concentration for all substances in solution ($\Delta H°$ ⟵ standard state

represented by superscript)

$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$ $\Delta H° = -2044$ kJ

$3CO_2(g) + 4H_2O(g) \longrightarrow C_3H_8(g) + 5O_2(g)$ $\Delta H° = + 2044$ kJ

Reverse <u>direction of reaction</u> reverse <u>sign of enthalpy</u>
(whatever you do to the reaction you also do to the enthalpy)

# HW 9.1: Calculating amount of heat released in a reaction:

$$2\ H_2\ (g) +\ O_2(g) \rightarrow\ 2\ H_2O\ (l) \qquad \Delta H° = -\ 571.6\ kJ$$

How much heat is released for:

a)   10.00 g of hydrogen gas with excess oxygen (FM H_2 = 2.02 g/mol)

$$10.00\ g\ H_2\ *\ \frac{1\ mol\ H_2}{2.02\ g\ H_2}\ *\ \frac{-571.6\ kJ}{2\ mol\ H_2}\ =\ -1414.85\ or\ -1415\ kJ$$
                                                              (heat released)

b) 5.500 mol of liquid water converted to hydrogen and oxygen gas
    (reversed RXN – change sign of reaction)

HW 9.1: Calculating amount of heat released in a reaction:
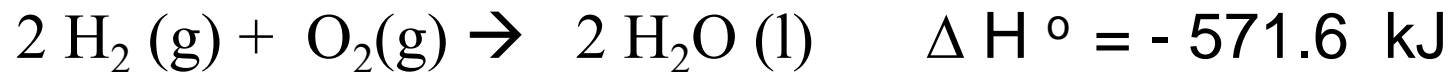
$$2\,H_2\,(g) + O_2(g) \rightarrow 2\,H_2O\,(l) \qquad \Delta H\,^\circ = -571.6\ \text{kJ}$$

How much heat is released for:

a)   10.00 g of hydrogen gas with excess oxygen (FM $H_2 = 2.02$ g/mol)

$10.00\ \text{g}\ \cancel{H_2}\ *\ \dfrac{1\ \text{mol}\ \cancel{H_2}}{2.02\ \text{g}\ \cancel{H_2}}\ *\ \dfrac{-571.6\ \text{kJ}}{2\ \text{mol}\ \cancel{H_2}}\ =\ -1414.85$ or -1415 kJ

(heat released)

b) 5.500 mol of liquid water is converted to hydrogen and oxygen gas (change sign – whatever do to reaction you do to enthalpy)

$5.500\ \text{mol}\ \cancel{\text{water (l)}}\ *\ \dfrac{571.6\ \text{kJ}}{2\ \text{mol}\ \cancel{\text{water(l)}}}\ =\ 1571.9\ \text{kJ} = 1572\ \text{kJ}$
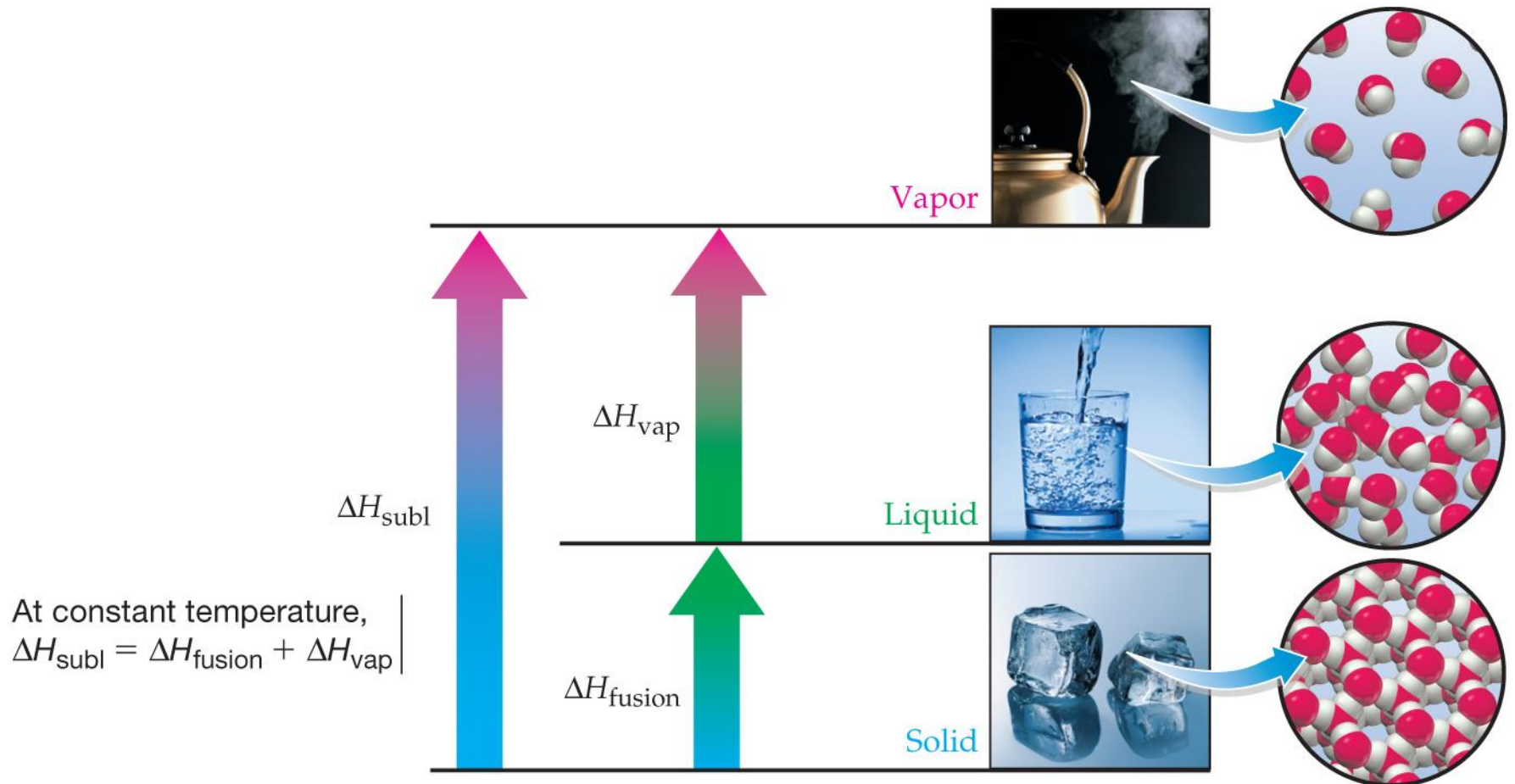
(heat absorbed)

Enthalpies of Physical and Chemical Change

Enthalpy of Fusion (ΔH_{fusion}): The amount of heat necessary to melt a substance without changing its temperature
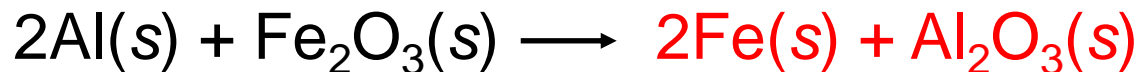
Enthalpy of Vaporization (ΔH_{vap}): The amount of heat required to vaporize a substance without changing its temperature

Enthalpy of Sublimation (ΔH_{subl}): The amount of heat required to convert a substance from a solid to a gas without going through a liquid phase

Enthalpies of Physical and Chemical Change

ΔH_{vap}

ΔH_{subl}

ΔH_{fusion}

Vapor

Liquid

Solid

At constant temperature,
$\Delta H_{subl} = \Delta H_{fusion} + \Delta H_{vap}$

Enthalpies of Physical and Chemical Change

$2Al(s) + Fe_2O_3(s) \longrightarrow 2Fe(s) + Al_2O_3(s)$

$\Delta H° = -852$ kJ

reverse reaction – change sign of enthalpy

Exothermic

$2Fe(s) + Al_2O_3(s) \longrightarrow 2Al(s) + Fe_2O_3(s)$
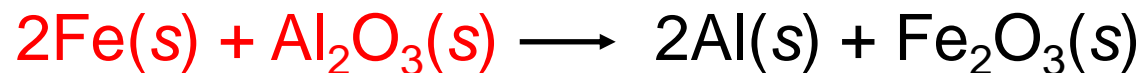
$\Delta H° = +852$ kJ

Endothermic

HW 9.2:   Endothermic vs. Exothermic

Endothermic - system gains heat from surrounding, heat flows into system (+ Δ H)

Exothermic -   system loses heat to surrounding, heat flows out of system (- Δ H)

Which of the following is Endothermic or Exothermic ?

boiling water – surrounding adds heat to boiling water (system) as it forms gas, + Δ H   endo

ice melting in ice coffee –

burning gasoline in a car engine -

End 1/8 Wed   A, C sect

HW 9.2:   Endothermic vs. Exothermic

Endothermic - system gains heat from surrounding, heat flows into system (+ Δ H)

Exothermic -   system loses heat to surrounding, heat flows out of system (- Δ H)

Which of the following is Endothermic or Exothermic ?

boiling water – surrounding adds heat to boiling water (system) as it forms, + Δ H   endo

ice melting in ice tea – heat flows into ice (system), + Δ H endo

burning gasoline (hydrocarbon like hexane or octane) in a car engine - reaction (system) produces heat – heat flows out of system, - Δ H, exothermic

# HW 9.3:   Enthalpy Calculation & Endo vs Exo Reaction

Given the following, if 10.0 grams of LiF (s) is dissolved in water, (a) would the temperature of the water (surroundings) rise to a higher number or lower down to a lower number ?   (b) What would be the enthalpy change for the given amount of Li F (s) ? (Formula Mass of LiF = 6.94 + 19.00 = 25.94 g/mol)

LiF (s) → Li^+ (aq)   + F^- (aq)   Δ H° = + 5.5 kJ

HW 9.3:   Enthalpy Calculation & Endo vs Exo Reaction

Given the following, if 10.0 grams of LiF (s) is dissolved in water, (a) would the temperature of the water rise to a higher number or lower down to a lower number ?   Water is surrounding. Δ H^o is positive – endo.   Surroundings (water) lower T

(b) What would be the enthalpy change for the given amount of Li F (s) ?   (FM of LiF = 6.94 + 19.00 = 25.94 g/mol)

LiF (s) →   Li$^+$ (aq)   + F$^-$ (aq) Δ H^o = + 5.5 kJ

10.0 grams LiF (s) * $\dfrac{\text{1 mol LiF (s)}}{\text{25.94 g LiF (s)}}$ * $\dfrac{\text{5.5 kJ}}{\text{1 mol LiF(S)}}$ =   2.12 kJ

Expansion Work – PV work (work = P ΔV)

$$C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(g)$$
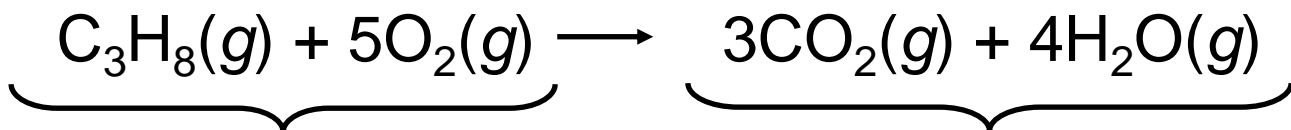
6 mol of gas

7 mol of gas

The **expansion in volume** that occurs during a reaction forces the piston outward against atmospheric pressure, P.

$P = \dfrac{F}{A}$

$P = \dfrac{F}{A}$

The amount of work done is equal to the pressure exerted in moving the piston (the opposite of atmospheric pressure, −P) times the volume change (ΔV).
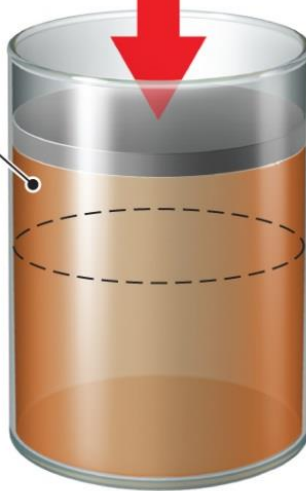
P * A = F

$$w = F \times d$$
$$= -P \times (A \times d)$$
$$= -P\Delta V$$

Δ V = A*d

Reaction

Before reaction
(initial state)

After reaction
(final state)

? Why is P negative ?
(a) work - comes out of system
    – so work is negative
(b) P by RXN – opposite in
    sign to P of atmosphere

Example: expansion work

Calculate the amount of work (kJ) done during a synthesis of ammonia in which the volume contracts from 8.6 Liters (initial) to 4.3 Liters (final) at a constant external pressure of 44 atm.

$w = - P \Delta V = - (44 \text{ atm}) * (4.3 \text{ Liters} - 8.6 \text{ Liters})$ wrong units

$J = (kg\, m^2)/s^2$ 1 atm = 101,325 Pa 1 Pa = 1 kg/m*s^2 1 L = 10^{-3} m^3

$$w = \left(-44 \text{ atm} * \frac{101325 \text{ Pa}}{\text{atm}} * \frac{1\, 1\, kg/m*s^2}{\text{Pa}} \right) \left(-4.3 \text{ L} * \frac{10^{-3}\, m^3}{\text{L}} \right)$$

$w = 19170.69 \, (kg\, m^2)/s^2 = 19170.69 \text{ J}$ Never Mind this Slide

$w = 19170.69 \text{ J} * \frac{1 \text{ kJ}}{1000 \text{ J}} = 19.2 \text{ kJ} = 19 \text{ kJ}$

all these conversions on periodic table that you get at all exams

Example: expansion work

Calculate the amount of work (kJ) done during a synthesis of ammonia in which the volume contracts from 8.6 Liters (initial) to 4.3 Liters (final) at a constant external pressure of 44 atm.

$w = -P \Delta V =$ - (44 atm)* (4.3 Liters – 8.6 Liters) wrong units

1 liter atm = 101.33 Joule ← memorize this
(use this slide instead)

w = - (44 atm)* (-4.3 liters) = 189.2 liter atm

w = 189.2 liter atm * $\dfrac{101.33 \text{ Joule}}{1 \text{ liter atm}}$ =   19171.636 Joule

w = 19171.636 Joule x $\dfrac{1 \text{ kJ}}{1000 \text{ J}}$ =   19 kJ
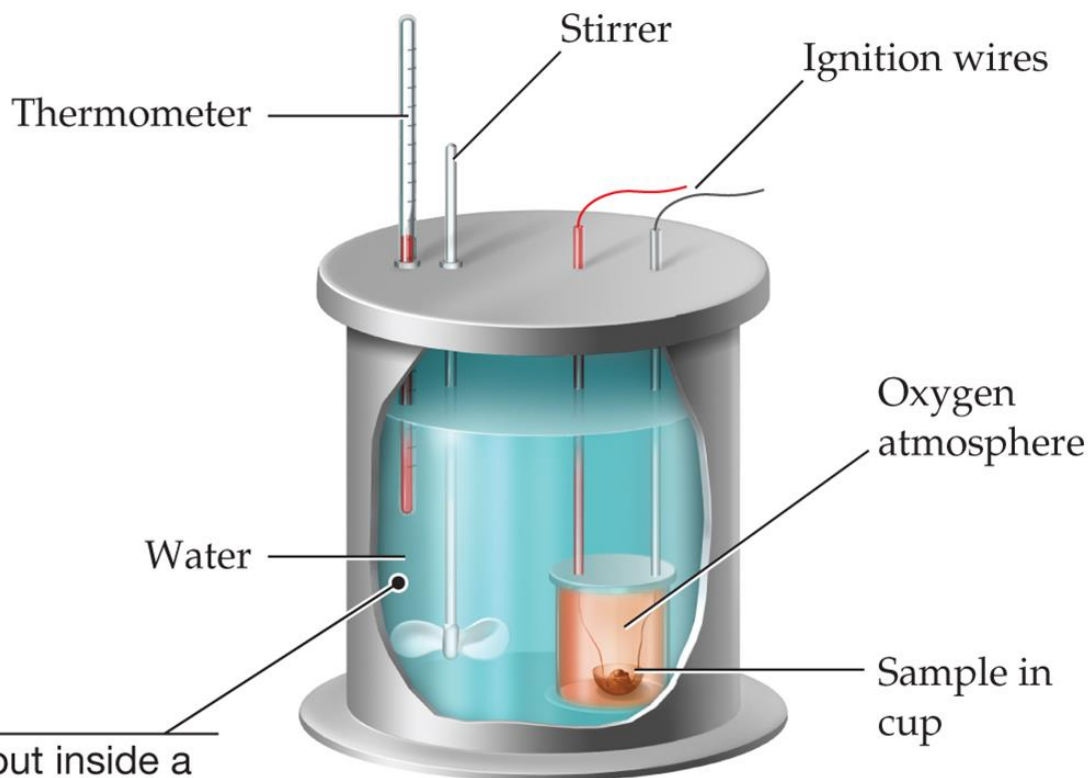
Calorimetry and Heat Capacity

Measure the heat flow at *constant pressure* (**ΔH**).

Thermometer

The reaction takes place inside an insulated vessel outfitted with a loose-fitting top, a thermometer, and a stirrer.

Stirrer

Insulated vessel

Reaction mixture
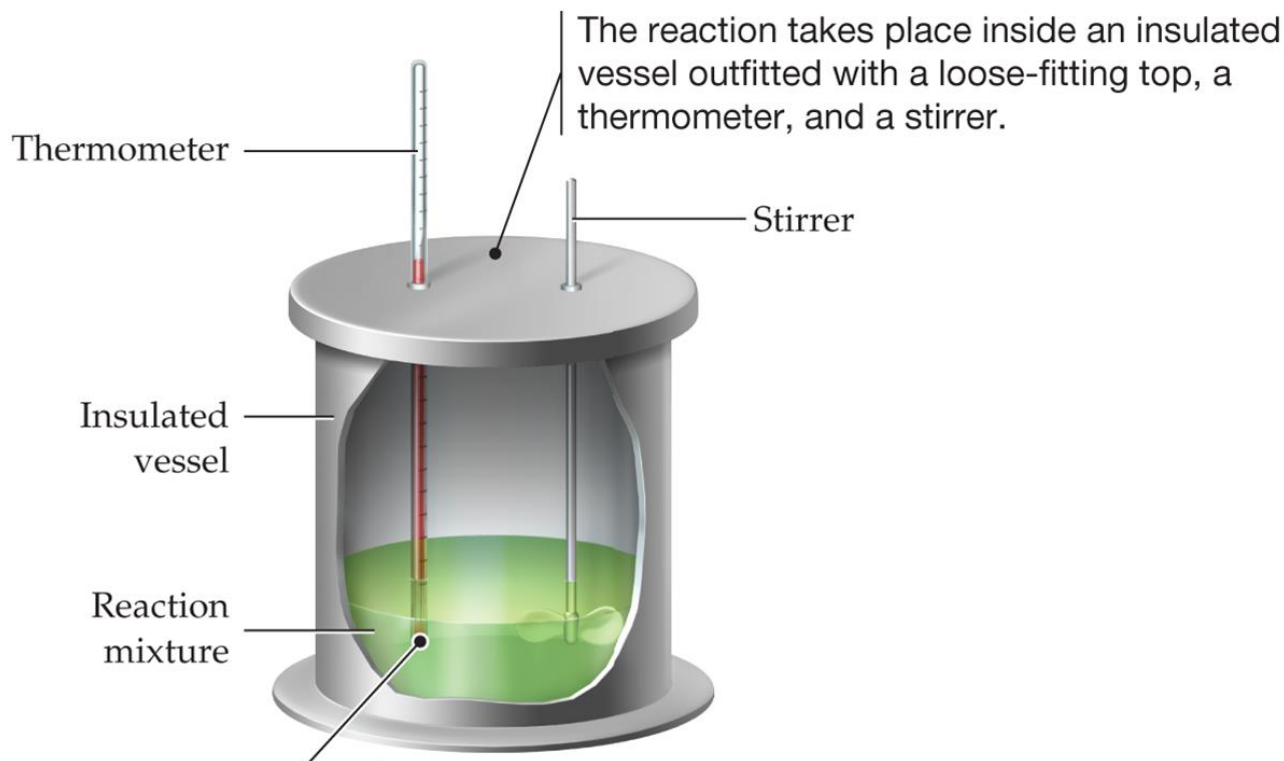
Measuring the **temperature change** that accompanies the reaction makes it possible to calculate ΔH.

Calorimetry and Heat Capacity

Measure the heat flow at *constant volume* (**ΔE**).

Thermometer

Stirrer

Ignition wires

Oxygen atmosphere

Water

Sample in cup

The reaction is carried out inside a steel bomb, and the heat evolved is transferred to the bomb and surrounding water, where the **temperature rise** is measured.

Calorimetry and Heat Capacity (look up heat capacity on chart) (constant P)

Heat Capacity (*C*): The amount of heat necessary to raise the temperature of an object or substance a given amount

$$C = \frac{q}{\Delta T} \qquad q = C \times \Delta T$$

Specific Heat (Capacity): The amount of heat required to raise the temperature of 1 g of a substance by 1 °C

$$q = (\text{Specific heat}) \times (\text{Mass of substance}) \times \Delta T$$

Calorimetry and Heat Capacity

Molar Heat Capacity (C_m): The amount of heat necessary to raise the temperature of 1 mol of a substance by 1 °C

$$q = C_m \times \text{Moles of substance} \times \Delta T$$

Calorimetry and Heat Capacity

$q = c \ m \ \Delta T$ $c = $ *specific heat capacity (J/g ^{o}C)*

$q = C_m \ mole \ \Delta T$ $C_m = $ *molar heat capacity J/mol^{o}C*

Watch units, put equations on to 3" x 5",
get chart with c or C_m values

Calorimetry and Heat Capacity

TABLE 9.1 Specific Heats and Molar Heat Capacities for Some Common Substances at 25 °C

Substance	Specific Heat (c) J/(g · °C)	Molar Heat Capacity (C_m) J/(mol · °C)
Air (dry)	1.01	29.1
Aluminum	0.897	24.2
Copper	0.385	24.4
Gold	0.129	25.4
Iron	0.449	25.1
Mercury	0.140	28.0
NaCl	0.859	50.2
Water(s)[a]	2.03	36.6
Water(l)	4.179	75.3

[a]At −11°C

Calorimetry and Heat Capacity

Assuming that a can of soda has the same specific heat as water, calculate the amount of heat (in kilojoules) transferred when one can (about 350 g) is cooled from 25 °C to 3 °C.

q = (Specific heat) × (Mass of substance) × ΔT

Specific heat = 4.18 $\dfrac{J}{g\,°C}$ Mass = 350 g

Temperature change = 3 °C − 25 °C = −22 °C

Heat evolved = $\dfrac{4.18\ J}{g\,°C}$ × 350 g × −22 °C = −32 000 J

−32 000 J × $\dfrac{1\ kJ}{1000\ J}$ = $\boxed{-32\ kJ}$

HW 9.4: Calorimetry and Heat Capacity

What is the specific heat of lead in J/g ^{o}C if it takes 97.2 J to raise the temperature of a 75.0 g block by 10.0^{o}C ?

$q = $ (specific heat) $\times$ (mass of substance) $\times \Delta T$
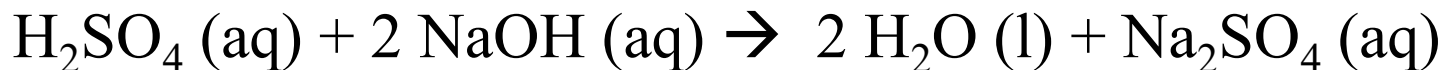
$q = c * m * \Delta T$

End 1/10 Friday
C section

HW 9.4: Calorimetry and Heat Capacity

What is the specific heat of lead in J/g ^{o}C if it takes 97.2 J to raise the temperature of a 75.0 g block by 10.0^{o}C ?

$q = $ (specific heat) $\times$ (mass of substance) $\times \Delta T$

$q = c * m * \Delta T$

Specific heat = ?   q = 97.2 J   mass = 75.0 g, ΔT = 10.0 ^{o}C

97.2 J = C * 75.0 g * 10.0 ^{o}C

$$C = \frac{97.2 \text{ J}}{75.0 \text{ g} * 10.0 \text{ }^oC} = \frac{0.1296 \text{ J}}{\text{g }^oC} = \frac{0.130 \text{ J}}{\text{g }^oC}$$

Ex: Calorimetry and Heat Capacity

Given the following reaction being done in a calorimeter (constant pressure rxn)

H_2SO_4 (aq) + 2 NaOH (aq) → 2 H_2O (l) + Na_2SO_4 (aq)

When 25.0 mL of 1.0 M H_2SO_4 is added to 50.0 mL of a 1.0 M NaOH at 25°C in a calorimeter,   The temperature of the solution rises to 33.9 °C.   If the specific heat of the solution is 4.18 J/g°C and density is 1.00 g/mL and the calorimeter does not absorb much heat. What is q ?

$q = c \; m \; \Delta T \quad c = J/(g \, {}^oC)$

(probably will not get question like this on exam or test)

Mass water = (25.0 mL + 50 mL) * 1.00 g/mL = m = 75.0 g

Will come back to finish problem later – want to cover other stuff for Quiz I

c = 4.18 J/(g °C)

ΔT = 33.9°C – 25°C = 8.9°C

q = (4.18 J/g°C)(75.0 g) (8.9°C) = 2790.15

Hess's Law

Hess's Law: The overall enthalpy change for a reaction is equal to the sum of the enthalpy changes for the individual steps in the reaction. (bc enthalpy is state function)
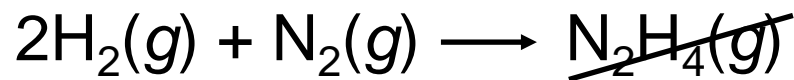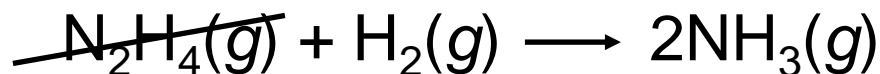
Haber Process
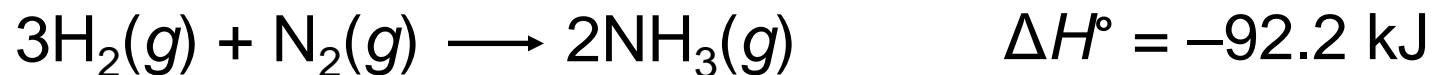
$$3H_2(g) + N_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H° = -92.2 \text{ kJ}$$

Hess's Law

Hess's Law: The overall enthalpy change for a reaction is equal to the sum of the enthalpy changes for the individual steps in the reaction.
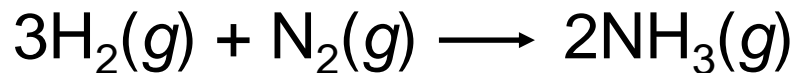
Multiple-Step Process

$$2H_2(g) + N_2(g) \longrightarrow \cancel{N_2H_4(g)} \qquad \Delta H°_1 = ?$$

$$\cancel{N_2H_4(g)} + H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta H°_2 = -187.6 \text{ kJ}$$

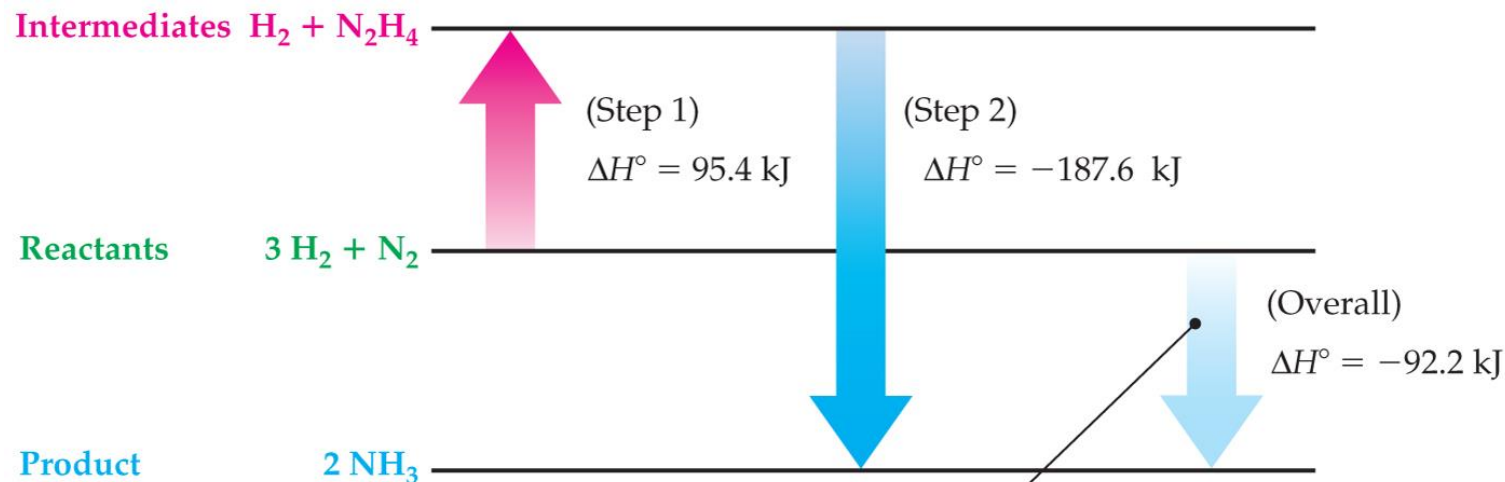$$\overline{3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)} \qquad \Delta H°_{1+2} = \quad -92.2 \text{ kJ}$$

Hess's Law

$$\Delta H^{\circ}_1 + \Delta H^{\circ}_2 = \Delta H^{\circ}_{1+2}$$

$$\Delta H^{\circ}_1 = \Delta H^{\circ}_{1+2} - \Delta H^{\circ}_2$$

$$= -92.2 \text{ kJ} - (-187.6 \text{ kJ}) = +95.4 \text{ kJ}$$

Intermediates $H_2 + N_2H_4$

(Step 1) $\Delta H^{\circ} = 95.4$ kJ

(Step 2) $\Delta H^{\circ} = -187.6$ kJ

Reactants $3 H_2 + N_2$

(Overall) $\Delta H^{\circ} = -92.2$ kJ

Product $2 NH_3$

The enthalpy change for the **overall reaction** equals the sum of the enthalpy changes for the individual Steps **1** and **2**, a statement known as Hess's law.
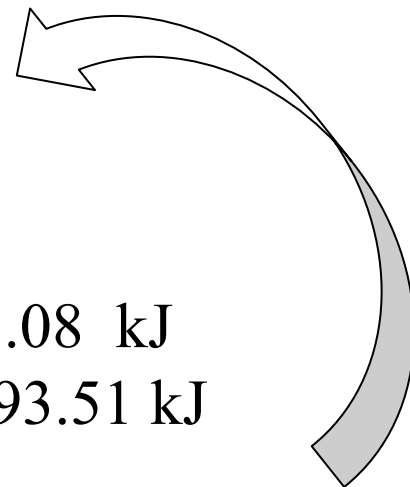
HW 9.5:   Hess's Law

Want enthalpy for the following reaction:

$CO \text{ (g)} + \frac{1}{2} O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)}$ $\Delta H^o = ?$

Have the following equations and enthalpies:

(a) $2 CO \text{ (g)} \rightarrow 2 C \text{ (s)} + O_2 \text{ (g)}$ $\Delta H^o = 221.08 \text{ kJ}$

(b) $CO_2 \text{ (g)} \rightarrow C \text{ (s)} + O_2 \text{(g)}$ $\Delta H^o = +393.51 \text{ kJ}$

Use **Hess's Law** to calculate the enthalpy for the reaction above.

HW 9.5:   Hess's Law

Want enthalpy for the following reaction:

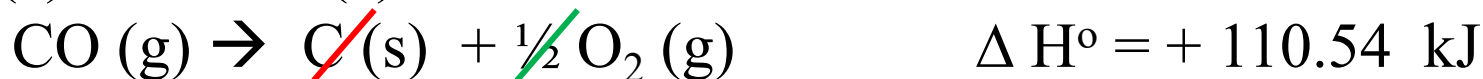$$CO (g) + \tfrac{1}{2} O_2 (g) \rightarrow CO_2 (g) \qquad \Delta H^o = ?$$

Have the following equations and enthalpies:

(a) $2 CO (g) \rightarrow 2 C (s) + O_2 (g) \qquad \Delta H^o = 221.08 \text{ kJ}$

(b) $CO_2 (g) \rightarrow C (s) + O_2(g) \qquad \Delta H^o = +393.51 \text{ kJ}$

Use **<u>Hess's Law</u>** to calculate the enthalpy for the reaction above.

(a) ½ of rxn (a)

$CO (g) \rightarrow C (s) + \tfrac{1}{2} O_2 (g) \qquad\qquad \Delta H^o = + 110.54 \text{ kJ}$

(b) Reverse direction of reaction

$C (s) + O_2(g) \rightarrow CO_2 (g) \qquad\qquad \Delta H^o = - 393.51 \text{ kJ}$

$CO (g) + \tfrac{1}{2} O_2 (g) \rightarrow CO_2 (g) \qquad \Delta H^o = - 282.97 \text{ kJ}$
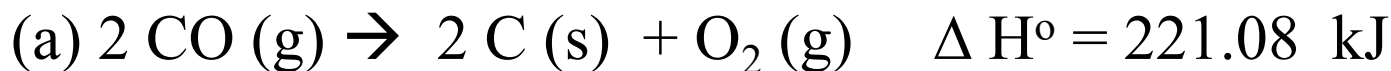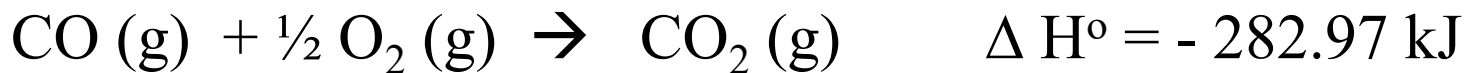
Standard Heats of Formation

Standard Heat of Formation (ΔH°_f): The enthalpy change for the formation of 1 mol of a substance in its standard state from its constituent elements in their standard states (textbook page A-8 has chart)

Standard states

$$C(s) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H^\circ_f = -74.8 \text{ kJ}$$

1 mol of a substance
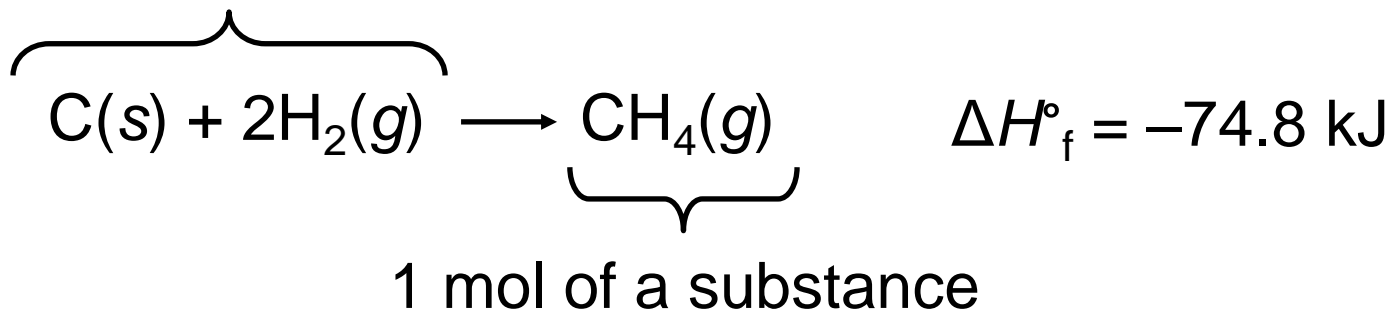
Standard Heats of Formation (look up chart)

TABLE 9.2   Standard Heats of Formation for Some Common Substances at 25 °C

Substance	Formula	$\Delta H°_f$ (kJ/mol)	Substance	Formula	$\Delta H°_f$ (kJ/mol)
Acetylene	$C_2H_2(g)$	227.4	Hydrogen chloride	$HCl(g)$	−92.3
Ammonia	$NH_3(g)$	−46.1	Iron(III) oxide	$Fe_2O_3(s)$	−824.2
Carbon dioxide	$CO_2(g)$	−393.5	Magnesium carbonate	$MgCO_3(s)$	−1095.8
Carbon monoxide	$CO(g)$	−110.5	Methane	$CH_4(g)$	−74.8
Ethanol	$C_2H_5OH(l)$	−277.7	Nitric oxide	$NO(g)$	91.3
Ethylene	$C_2H_4(g)$	52.3	Water (g)	$H_2O(g)$	−241.8
Glucose	$C_6H_{12}O_6(s)$	1273.3	Water (l)	$H_2O(l)$	−285.8

Standard Heats of Formation – generalized equation

$$\Delta H° = \Delta H°_f \text{ (Products)} - \Delta H°_f \text{ (Reactants)}$$

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$
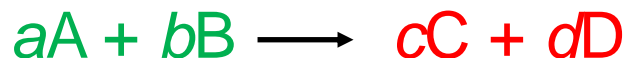
This is a generalized balanced chemical reaction where a, b, c, d are the coeffients for the balanced chemical reaction.

$$\Delta H° = [c\,\Delta H°_f \text{ (C)} + d\,\Delta H°_f \text{ (D)}] - [a\,\Delta H°_f \text{ (A)} + b\,\Delta H°_f \text{ (B)}]$$

Products   Reactants

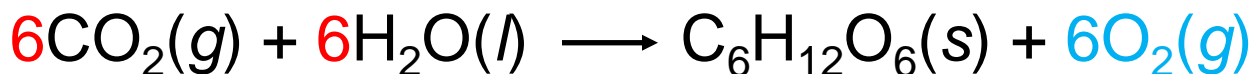# Standard Heats of Formation

Using standard heats of formation, calculate the standard enthalpy of reaction for the photosynthesis of glucose ($C_6H_{12}O_6$) and O_2 from CO_2 and liquid H_2O.

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g)$$
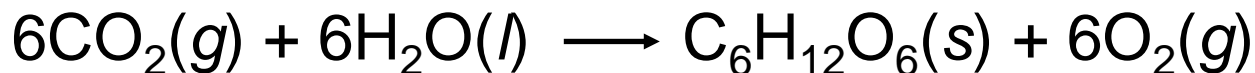
$$\Delta H^\circ = \text{?}$$

Standard Heats of Formation – use chart

$$6CO_2(g) + 6H_2O(l) \longrightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

$\Delta H° = ?$

$\Delta H° = [\Delta H°_f (C_6H_{12}O_6(s))] -$

$\qquad [6 \Delta H°_f (CO_2(g)) + 6 \Delta H°_f (H_2O(l))]$

$\Delta H° = [(1 \text{ mol})(-1260 \text{ kJ/mol})] -$

$\qquad [(6 \text{ mol})(-393.5 \text{ kJ/mol}) + (6 \text{ mol})(-285.8 \text{ kJ/mol})]$

$\Delta H° = \boxed{2816 \text{ kJ}}$

$\Delta H°_f[O_2(g)] = \text{zero}$ because most stable form of element
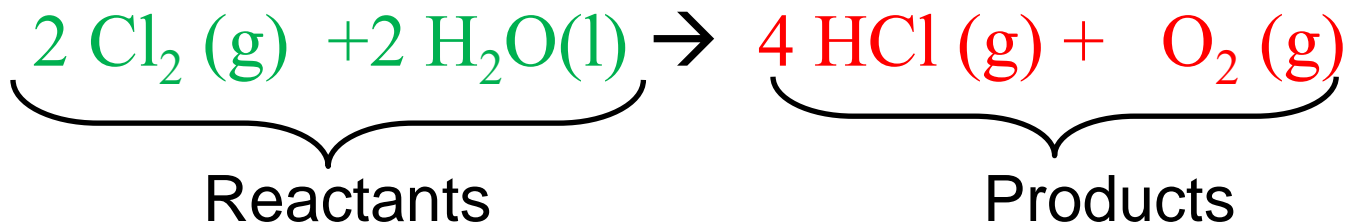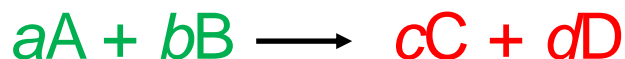
$\Delta H°_f = \text{zero}$
Most stable form of elements Fe(s), $H_2(g)$

end 1/13/20 Monday A section, end 1/14 Tuesday C section after HW 9.6 on next slide
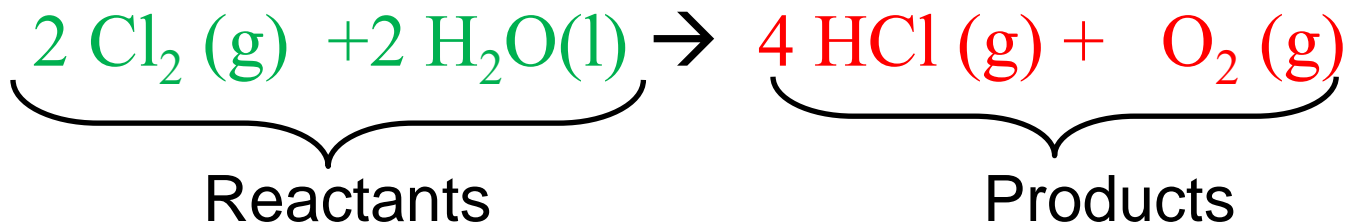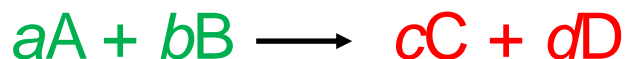
HW 9.6: Standard Heats of Formation

$$\Delta H° = \Delta H°_f \text{ (Products)} - \Delta H°_f \text{ (Reactants)}$$

$$a\text{A} + b\text{B} \longrightarrow c\text{C} + d\text{D}$$

$$2\,\text{Cl}_2\,(g) + 2\,\text{H}_2\text{O}(l) \rightarrow 4\,\text{HCl}\,(g) + \text{O}_2\,(g)$$

Reactants   Products

$\Delta H°_f\,[\text{HCl}\,(g)] = -92.31\text{ kJ/mol}$ from chart Appendix B
$\Delta H°_f\,[\text{H}_2\text{O}\,(l)] = -285.8\text{ kJ/mol}$ from your text

HW 9.6: Standard Heats of Formation – generalized equation

$$\Delta H° = \Delta H°_f \text{ (Products)} - \Delta H°_f \text{ (Reactants)}$$

$$aA + bB \longrightarrow cC + dD$$

$$2\,Cl_2\,(g) + 2\,H_2O(l) \rightarrow 4\,HCl\,(g) + O_2\,(g)$$

Reactants   Products

$$\Delta H° = \{[4\,\Delta H°_f\,(HCl\,(g)\,)] + [\Delta H°_f\,(O_2(g))]\}$$
$$- \{\,[2\,\Delta H°_f\,(Cl_2(g)\,)] + [2\,\Delta H°_f\,(H_2O\,(l)\,)]\}$$

$$\Delta H° = \{[4\,(-92.31\,)] + [\,(0.00)]\} - \{\,[2\,(0.00\,)] + [2\,(-285.8\,)]\}$$

$$\Delta H° = \{4\,(-92.31\,)\} - \{[2\,(-285.8\,)]\}$$

$$\Delta H° = \{4\,(-92.31\,)\} - \{[2\,(-285.8\,)]\} =$$

$$-369.24 + 571.6 = 202.4 kJ$$

End Quiz 1 -
Start Quiz 2 after this slide

Bond Dissociation Energies

**Bond dissociation energies** are standard enthalpy changes for the corresponding bond-breaking reactions.

TABLE 7.2	Average Bond Dissociation Energies, D (kJ/mol)								
H—H	436[a]	C—H	410	N—H	390	O—F	180	I—I	151[a]
H—C	410	C—C	350	N—C	300	O—Cl	200	S—F	310
H—F	570[a]	C—F	450	N—F	270	O—Br	210	S—Cl	250
H—Cl	432[a]	C—Cl	330	N—Cl	200	O—I	220	S—Br	210
H—Br	366[a]	C—Br	270	N—Br	240	O—N	200	S—S	225
H—I	298[a]	C—I	240	N—N	240	O—O	180		
H—N	390	C—N	300	N—O	200	F—F	159[a]		
H—O	460	C—O	350	O—H	460	Cl—Cl	243[a]		
H—S	340	C—S	260	O—C	350	Br—Br	193[a]		

Multiple covalent bonds[b]

C=C	728	C≡C	965	C=O	732	O=O	498[a]	N≡N	945[a]

[a]Exact value.

[b]We'll discuss multiple covalent bonds in Section 7.5.

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Bond Dissociation Energies

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$$
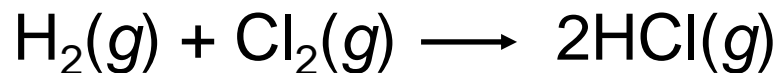
$\Delta H° = D(\text{Reactant bonds}) - D(\text{Product bonds})$
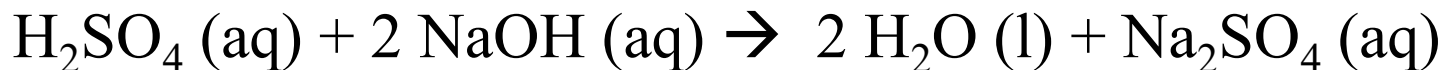
$\Delta H° = (D_{H-H} + D_{Cl-Cl}) - (2D_{H-Cl})$

$\Delta H° = [(1 \text{ mol})(436 \text{ kJ/mol}) + (1 \text{ mol})(243 \text{ kJ/mol})] -$

$$(2 \text{ mol})(432 \text{ kJ/mol})$$

$\Delta H° = \boxed{-185 \text{ kJ}}$

Ex: Calorimetry and Heat Capacity

Given the following reaction being done in a calorimeter (constant pressure rxn)

H_2SO_4 (aq) + 2 NaOH (aq) → 2 H_2O (l) + Na_2SO_4 (aq)

When 25.0 mL of 1.0 M H_2SO_4 is added to 50.0 mL of a 1.0 M NaOH at 25°C in a calorimeter, The temperature of the solution rises to 33.9 °C. If the specific heat of the solution is 4.18 J/g°C and density is 1.00 g/mL and the calorimeter does not absorb much heat. What is q ?

(probably will not get question like this on exam or test)

$q = c\ m\ \Delta T\quad c = J/(g\,°C)$

Mass water = (25.0 mL + 50 mL) * 1.00 g/mL = m = 75.0 g

Will come back to finish problem later – want to cover other stuff for Quiz I

c = 4.18 J/(g °C)

ΔT = 33.9°C – 25°C = 8.9°C

q = (4.18 J/g°C)(75.0 g) (8.9°C) = 2790.15

ex: Calorimetry and Heat Capacity (continue)

Given the following reaction being done in a calorimeter (constant pressure rxn)

H_2SO_4 (aq) + 2 NaOH (aq) → 2 H_2O (l) + Na_2SO_4 (aq)

When 25.0 mL of 1.0 M H_2SO_4 is added to 50.0 mL of a 1.0 M NaOH at 25°C in a calorimeter,   The temperature of the solution rises to 33.9 °C.   If the specific heat of the solution is 4.18 J/g°C and density is 1.00 g/mL and the calorimeter does not absorb much heat. What is q ?   What is ΔH for the RXN as written for 1 mol H_2SO_4 ?

q = (4.18 J/g°C)(75.0 g) (8.9°C) = 2790.15 J

(probably will not get question like this on exam or test)

Is q = Δ H ?   (a) Is heating water & calorimeter the reaction ? OR
(b) Is the reaction the neutralization reaction ?
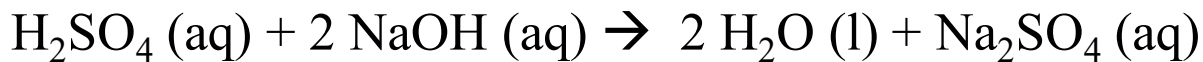
(a) heating water & calorimeter = surroundings (2790.15 J)
        q (for surroundings) ↘ ΔH (for reaction, system) = 2790.15 J

(b) reaction: H_2SO_4 + 2 NaOH = system (-2790.15 J for 25.0 mL of
1.0 M H_2SO_4)   q (for system) = Δ H = -q (surrounding) = -2790.15J

ex: Calorimetry and Heat Capacity (continue)

Given the following reaction being done in a calorimeter (constant pressure rxn)

H_2SO_4 (aq) + 2 NaOH (aq) → 2 H_2O (l) + Na_2SO_4 (aq)

When 25.0 mL of 1.0 M H_2SO_4 is added to 50.0 mL of a 1.0 M NaOH at 25°C in a calorimeter, The temperature of the solution rises to 33.9 °C. If the specific heat of the solution is 4.18 J/g°C and density is 1.00 g/mL and the calorimeter does not absorb much heat. What is q ? What is ΔH for the RXN as written for 1 mol H_2SO_4 ?

(probably will not get question like this on exam or test)

q = (4.18 J/g°C)(75.0 g) (8.9°C) = 2790.15 J

our q is for 25.0 mL of 1 M H_2SO_4

for NOT 1 mol but for   25.0 mL * $\dfrac{1.0 \text{ mol } H_2SO_4}{1000 \text{ mL}}$ = 0.025 mol H_2SO_4

1.0 mol H_2SO_4 * $\dfrac{- 2790.15 \text{ J}}{0.025 \text{ mol } H_2SO_4}$ = -111606 J/mol = - 111.6 kJ/mol ΔH for RXN

End 1/15 A section

An Introduction to Entropy

Spontaneous Process: A process that, once started, proceeds on its own without a continuous external influence (going downhill in energy)

An Introduction to Entropy

Entropy (*S*): The amount of molecular randomness in a system

solid (low S) → liquid (medium S) → gas (high S)

Liquids have more randomness and higher entropy than **solids**.

Gases have more randomness and higher entropy than **liquids**.

Less randomness, lower entropy → More randomness, higher entropy
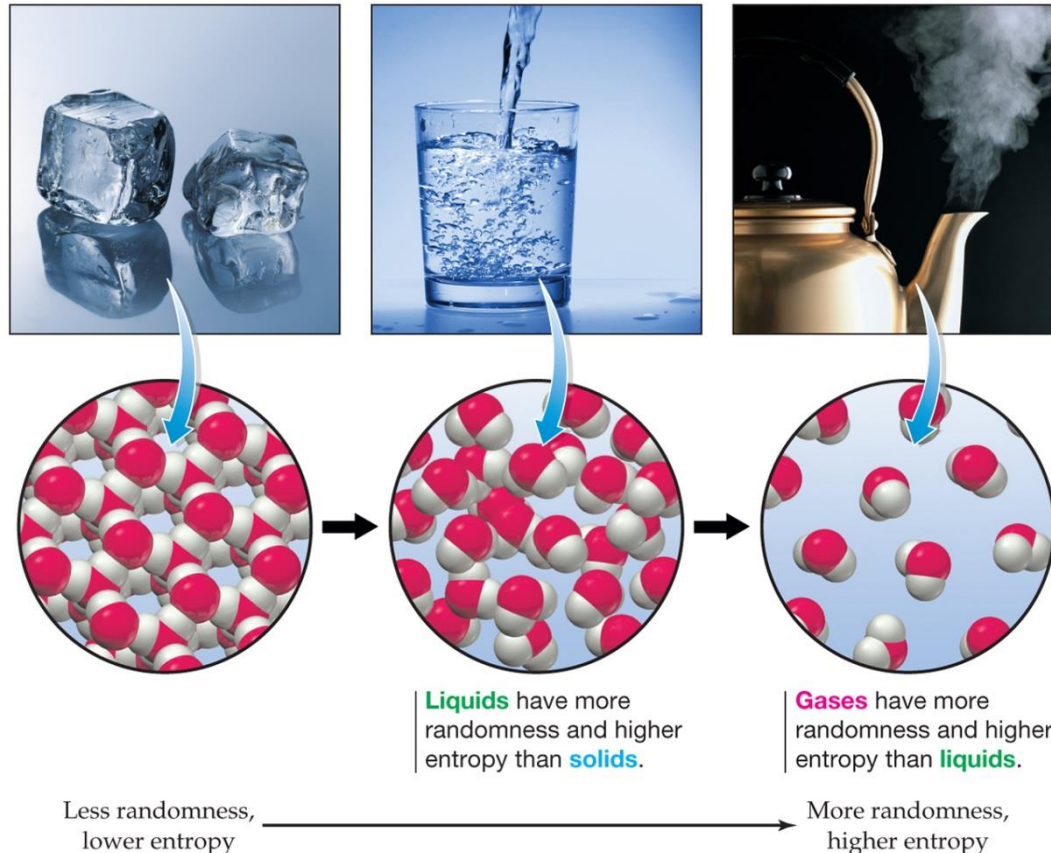
An Introduction to Entropy

Spontaneous processes are (memorize this)
- favored by a decrease in H (negative ΔH).
(reaction spontaneously releases heat)
- favored by an increase in S (positive ΔS).
(reaction spontaneously becomes more disordered)

Nonspontaneous processes are
- favored by an increase in H (positive ΔH).
- favored by a decrease in S (negative ΔS).

An Introduction to Free Energy

Gibbs Free-Energy Change (ΔG)

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

Enthalpy of
Reaction
kJ/mol
(- ΔH spontaneous)
reaction releases heat

Temperature
(in kelvin)

Entropy
Change
kJ/mol
(+ΔS spontaneous)
reaction more disordered

Spontaneous   ΔG = negative
(rxn goes →)   ΔH = negative
(← nonspontaneous) Δ S = positive

End 1/15 Wed
C section

An Introduction to Free Energy

Gibbs Free-Energy Change (Δ*G*)

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

high T: ΔS decides
low   T: ΔH decides

Δ*G* < 0   Process is spontaneous. (rxn goes →)

Δ*G* = 0   Process is at equilibrium
(neither spontaneous nor nonspontaneous).

Δ*G* > 0   Process is nonspontaneous.   (rxn goes ←)

HW 9.7: An Introduction to Free Energy

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

Spontaneous ΔG = negative
(rxn goes →) ΔH = negative
 (← nonspontaneous) ΔS = positive

Complete the following table:

ΔG	ΔH	Δ S	T	spontaneous (yes,no,maybe)
____	+	+	large	_____
____	-	+	small	_____
____	-	-	large	_____
____	-	-	small	_____

HW 9.7: An Introduction to Free Energy

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

Spontaneous
(rxn goes →)
  (← nonspontaneous)

ΔG = negative
ΔH = negative
ΔS = positive

Complete the following table:

End 1/17F
A & C
section

ΔG	ΔH	ΔS	T	spontaneous (yes,no,maybe)
neg	+	+	large	spontaneous
neg	-	+	small	spontaneous
pos	-	-	large	not spontaneous
neg	-	-	small	spontaneous

HW 9.8: An Introduction to Free Energy

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

Spontaneous ΔG = negative
(rxn goes →) ΔH = negative
 (← nonspontaneous) ΔS = positive

If ΔH = 42 kJ and ΔS = -111 J/K at 400 K, (a) what is ΔG ?

(b) Is the reaction spontaneous ?

HW 9.8: An Introduction to Free Energy

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

Spontaneous ΔG = negative
(rxn goes →) ΔH = negative
 (← nonspontaneous) ΔS = positive

If ΔH = 42 kJ and ΔS = -111 J/K at 400 K, (a) what is ΔG ?

ΔG = 42 kJ* 1000 J/kJ - (400K) (- 111 J/K) = 42000 J + 44400 J
     =   86400 J = 86.4 kJ

(b) Is the reaction spontaneous ?   no