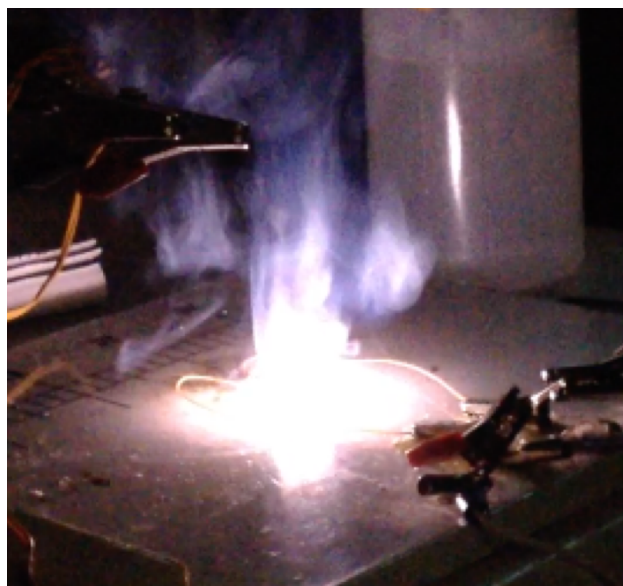


Chapter Six



Energy Relationships in Chemical Reactions

Energy (U): Capacity to Do Work

Some types of energy:

- **Radiant**

- Energy from the sun



$$\text{Energy} = \text{force} \times \text{distance}$$

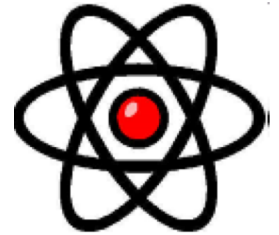
$$= \text{N} \times \text{m}$$

$$= \text{kg m}^2 / \text{s}^2$$

$$= \text{kg m}^2 \text{ s}^{-2}$$

- **Nuclear**

- Energy stored in the nucleus of an atom



- **Thermal**

- Energy associated with temperature
- Type of kinetic energy: due to molecular movement



- **Chemical**

- Energy stored in chemical bonds
- Type of potential energy: due to position of an object



Thermochemistry

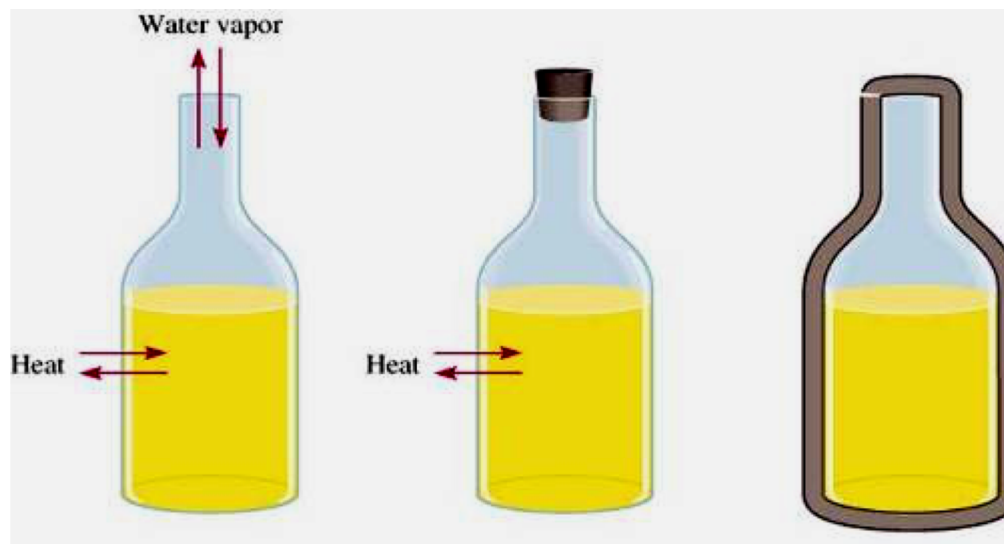
Study of heat change in chemical reactions

System: The part of the universe being studied

Open: Energy & matter exchange with surroundings

Closed: Only energy exchange with surroundings

Isolated: No energy or matter exchange - rare



Surroundings: Part of the universe not being studied

Heat Transfer in a System

Heat (q): Transfer of energy due to temp. difference

Exothermic Reaction: System gives off heat (Exiting)

Ex: Methane Burning: $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$

Bonds stronger in $\text{CO}_2 + \text{H}_2\text{O}$ than in $\text{CH}_4 + \text{O}_2$

- Energy is absorbed when bonds break & released when bonds form
- In this case more energy released than absorbed
- Heat goes from system to surroundings

Endothermic Reaction: System gains heat (Entering)

Ex: Ice Melting: $\text{H}_2\text{O (s)} \rightarrow \text{H}_2\text{O (l)}$

- Need energy to disrupt attractions between H_2O molecules
- Heat goes from surroundings into the system

Thermodynamics – Study of the conversions
between heat & energy

State vs. Path Functions

Δ = change

State of a system:

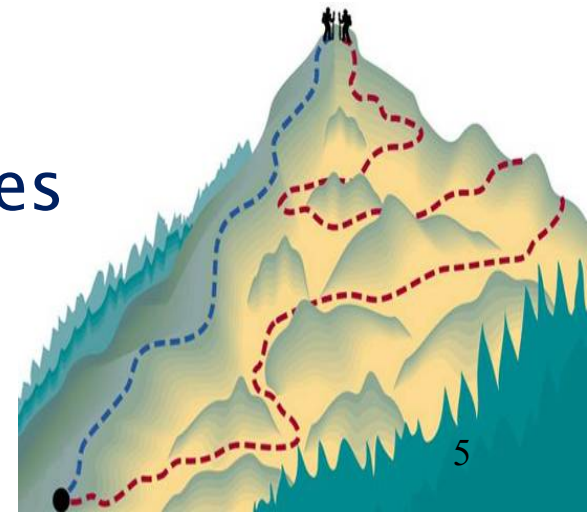
- Describes specific conditions/macrosscopic properties
 - Composition, temp., pressure, energy, volume
- ex: Potential energy of ball at the top of the mountain

State functions:

- Properties defined by $\Delta_{\text{final}} - \Delta_{\text{initial}}$ values only
→ process doesn't matter
- ex: Height of mountain

Path functions:

- $\Delta_{\text{final}} - \Delta_{\text{initial}}$ values vary by process
 - Heat, work: interdependent variables
- ex: the actual distance travelled by ball on its trip to the bottom of the mountain.



First Law of Thermodynamics

Energy can be converted from 1 form to another
but cannot be created or destroyed

$$\Delta U_{\text{system}} = U_{\text{final}} - U_{\text{initial}}$$

Internal Energy of System: $U_{\text{system}} = U_{\text{kinetic}} + U_{\text{potential}}$

Kinetic energy: Amount of molecular motion
Associated with temperature

Potential energy: Energy stored in bonds
Strength of chemical bonds

When studying a reaction, cannot separate kinetic
& potential energy – measure total energy instead

For chemical reactions: $\Delta U_{\text{reaction}} = U_{\text{products}} - U_{\text{reactants}}$

Internal Energy: Work and Heat

Energy transfer - caused by changes in heat & work in a system

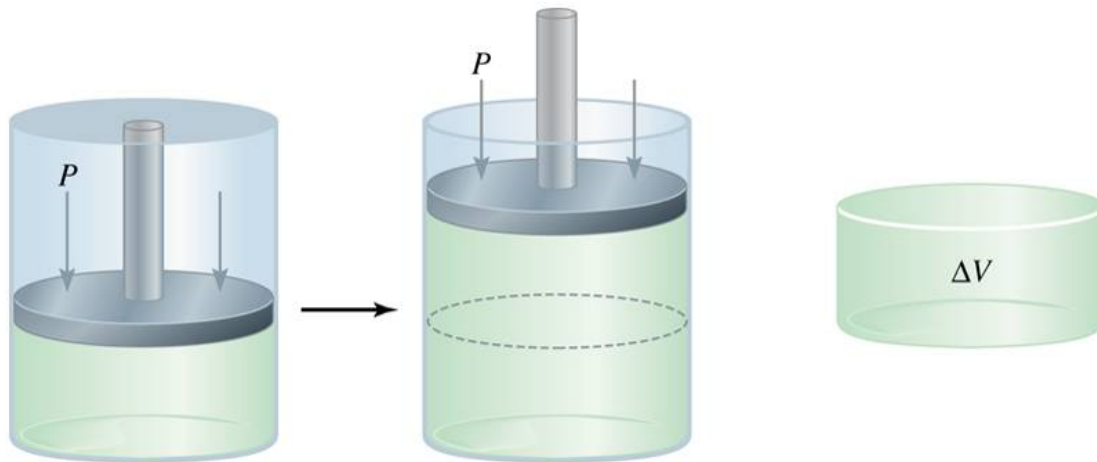
$$\Delta U_{\text{system}} = q + w$$

$$\text{Work (w)} = \text{force} \times \text{distance} = -P\Delta V$$

Work is needed to expand a system against its surroundings

Negative work (-w): System loses energy to surroundings

Positive work (+w): System gains energy from surroundings



$$\text{Work (w)} = -P\Delta V$$

$$\Delta V = V_f - V_i$$

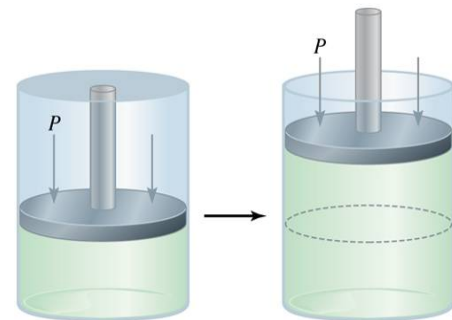
For this situation:
 $+ \Delta V$

Therefore: $-W$

$$1 \text{ L} \times \text{atm} = 101.32 \text{ J}$$

Work and Heat

A gas expands in volume from 2.000 L to 4.000 L at STP. 350.0 J of energy are needed to maintain the new conditions.



- a. Calculate work (J) done against a vacuum & against a pressure of 1 atm. (A = 0.000 J, -202.6 J)

*Note that work is reported in J, not L x atm.

- b. Calculate the heat required for each system.

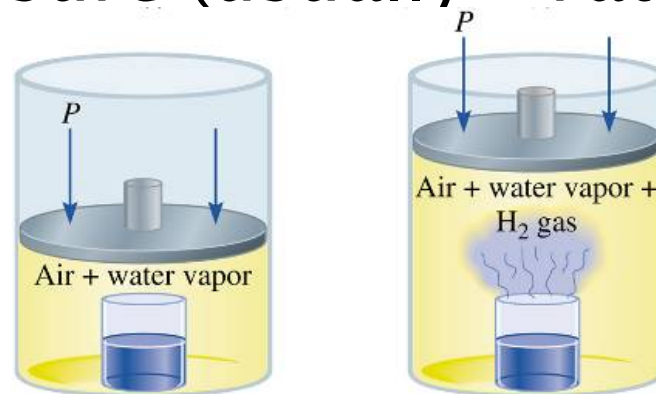
(A = 350.0 J; 552.6 J)

Enthalpy of Chemical Reactions

For systems at constant pressure (usually $\sim 1 \text{ atm}$):

$$\Delta U = q + w = q_p - P\Delta V$$

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



Enthalpy: (H) Experimentally measured & tabulated

- Can think of as heat of a reaction

At constant pressure:

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

Assume negligible volume change: $\Delta H = \Delta U = q_p$

There will be slight differences between ΔH and ΔU , but in many cases they are small enough to be considered negligible

Ways of Calculating Enthalpy/Heat/Energy exchange

$$q = ms\Delta T$$

$$q = C\Delta T$$

Experimental

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

$$\Delta U_{\text{system}} = q + w$$

$$\Delta U_{\text{system}} = U_{\text{final}} - U_{\text{initial}}$$

Theoretical

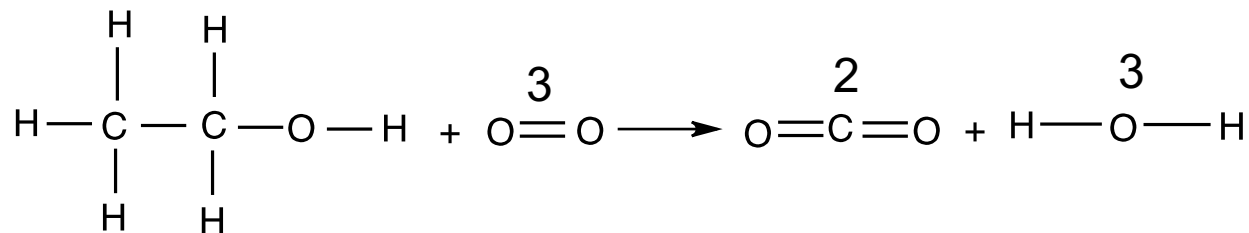
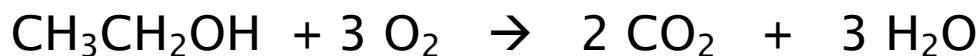
$$\Delta H_{\text{reaction}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$$

$$\Delta H_{\text{reaction}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$$

To determine which formula to use – look at information given in the problem!

Why is there an enthalpy change during chemical reactions?

Theoretical Calculation: $\Delta H = E_{in} - E_{out}$ (Chapter 9)



C-C Bond = 80 kcal/mole

C-H Bond = 100 kcal/mole

C-O Bond = 90 kcal/mole

O=O Bond = 120 kcal/mole

O-H Bond = 110 kcal/mole

C=O Bond = 180 kcal/mole

E_{in} :

1 C-C bond x 80 kcal/mol = 80 kcal/mol
5 C-H bonds x 100 kcal/mol = 500 kcal/mol
1 C-O bond x 90 kcal/mol = 90 kcal/mol
1 O-H bond x 110 kcal/mol = 110 kcal/mol
3 O=O bond x 120 kcal/mol = 360 kcal/mol

1140 kcal/mol

E_{out} :

2x2 C=O bonds x 180 kcal/mol = 720 kcal/mol
3x2 O-H bonds x 110 kcal/mol = 660 kcal/mol

1380 kcal/mol

$$\begin{aligned} \Delta H &= E_{in} - E_{out} \\ &= 1140 \text{ kcal/mol} - 1380 \text{ kcal/mol} \\ &= -240 \text{ kcal/mol} \end{aligned}$$

Enthalpy of Reaction ($\Delta H = q_{\text{rxn}}/\text{mol}$)

Amount of heat exchanged between system and surroundings during a chemical reaction

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

Exothermic Reactions

- Temperature increases in an isolated system.
- Heat released to surroundings is treated as a product
- ΔH is negative



Endothermic Reaction

- Temperature decreases in an isolated system.
- Heat absorbed by system is treated as a reactant
- ΔH is positive



State function: Independent of path

Rules for Working with Heat and Enthalpy

1. Make same changes to enthalpy as to # moles
If decrease or increase reactants and products, do the same for ΔH



$$\Delta H = -197.8 \text{ kJ} / 2 \text{ mol SO}_3(\text{g}) \quad \Delta H = -98.9 \text{ kJ} / 1 \text{ mol SO}_3(\text{g})$$

2. Reverse the reaction, reverse sign of ΔH



These rules will allow you to calculate the ΔH for any amount of product or reactant

Calculate how much heat is required to **decompose** 15.0g NO₂(g) according to this reaction:



Info Provided:

Calculate molar mass of NO₂ - convert mass to moles NO₂.

Use coefficient & moles NO₂ present to find ΔH for 15.0 g.

Calculating ΔH Via Experiment: Calorimetry

Calorimetry: Measurement of heat changes

Calorimeter: Device to measure heat (ΔT) produced by a chemical reaction

- $\Delta T = T_{\text{final}} - T_{\text{initial}}$
- Units: generally $^{\circ}\text{C}$

Specific Heat (s): Heat needed to raise T of 1 **gram** by 1°C .

- $s = q / (m \times \Delta T)$ $s_{\text{water}} = 4.184 \text{ J/g}^{\circ}\text{C}$
- Units: $\text{J/g}^{\circ}\text{C}$ or $\text{cal/g}^{\circ}\text{C}$ $= 1 \text{ cal/g}^{\circ}\text{C}$

Heat capacity (C): Quantity of heat needed to raise T by 1°C

- $C = m \times s$
- Units: $\text{J/}^{\circ}\text{C}$ or J/K

Heat of Reaction (q_{rxn})

- $q = m \times s \times \Delta T$ or $q = C \Delta T$
- Units: J

Commonly Used Specific Heats

Substance	Specific Heat (J/g · °C)
Al	0.900
Au	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu	0.385
Fe	0.444
Hg	0.139
H ₂ O	4.184
C ₂ H ₅ OH (ethanol)	2.46

Calorimetry Experiments

During the experiment, heat is transferred from the reaction (system) to the water (surroundings)

1. Measure ΔT of water
2. Use $q = ms\Delta T$ to calculate the heat gained or lost by the water
3. Heat gained by the water is lost by the system; heat lost by the water is gained by the system:

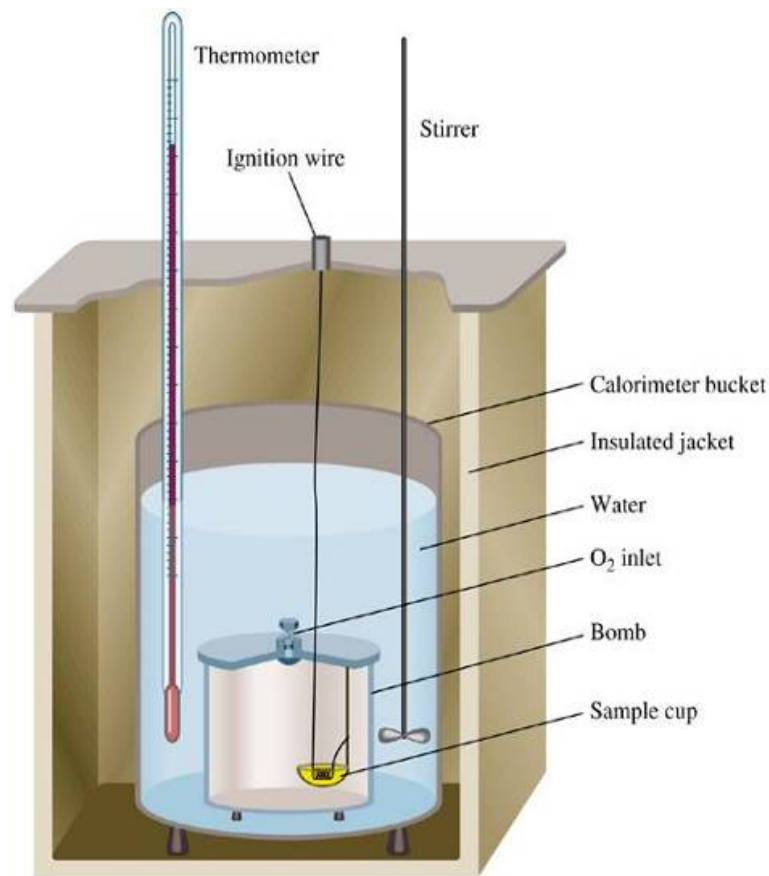
$$-q_{\text{rxn}} = q_{\text{H}_2\text{O}}$$

4. Use q_{rxn} to determine information about system variables: $q_{\text{rxn}} = m_{\text{sys}} \times s_{\text{sys}} \times \Delta T_{\text{sys}}$

Always have 2 sets of variables!

1 for water (surroundings)

1 for reaction (system)



A 30.0g sample of metal is heated to 100.0°C by placing it in a boiling water bath. The metal is removed from the boiling water, and placed in 25.0g of water at 22.0°C. The final temp was 27.6°C, what is the specific heat of the metal? $S_{\text{H}_2\text{O}} = 4.18 \text{ J/g}^\circ\text{C}$

What is your equation?

What info is provided?

Solve for $q_{\text{H}_2\text{O}}$ ($q_{\text{H}_2\text{O}} = -q_{\text{metal}}$)

Use formula for q_{metal} to solve for s_{metal}

$$A = 0.269 \text{ J/g}^\circ\text{C}^{18}$$

Heat Evolved During a Chemical Reaction

Reaction conducted in a Styrofoam cup calorimeter

- The calorimeter does not absorb or give off heat.
- Heat absorbed by the solution in the calorimeter (q_{cal}) is the heat that has been given off by the chemical reaction ($-q_{\text{rxn}}$)

Two solutions are mixed in the calorimeter

40.0 mL of 1.00 M KOH(aq)

40.0 mL of 0.500 M $\text{H}_2\text{SO}_4(\text{aq})$

T_i of both solutions = 21.00°C

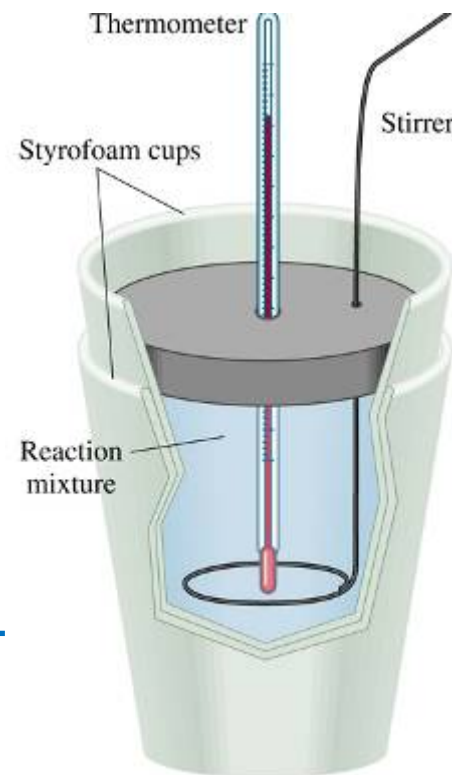
Data on final solution

Density: 1.02 g/mL

S.H.: 4.00 J/g $^\circ\text{C}$

Volume: 80.0 mL

Temp.: 27.85°C



Calculate the enthalpy change, ΔH , of this reaction per mole of H_2O formed.

1. What is the chemical reaction?



$$\Delta H_{\text{rxn}} = q_{\text{rxn}} = -q_{\text{water}}$$

$$q = m \times s \times \Delta T$$

2. What information is given?

Initial Information:

40.0 mL of 1.00 M KOH(aq)

40.0 mL of 1.00 M H_2SO_4 (aq)

T_i of both solutions = 21.00°C

Final information:

Density: 1.02 g/mL

Volume: 80.0 mL

S.H.: 4.00 J/g $^\circ\text{C}$ (not just H_2O)

Temp: 27.85°C

Note: ΔH calculated from calorimetry is heat that was transferred into the water in the CALORIMETER, not water from the chemical reaction!!! Amount of heat generated here is for grams of reactants used, not per mole H_2O ! Since you need ΔH per mole, you need to calculate how many moles of water you produced.

Calculating the ΔH per mole H_2O , con't

Calculate heat of reaction (q) from experiment. The calculated q_{H_2O} will be per gram of reactants used.

Calculate the # of moles of water produced in the reaction. Need to find LR!

Calculate ΔH per 1 mole of water produced. Remember that $q_{H_2O} = -q_{rxn}$.

Typical Heats of Reactions

TABLE 6.3 Heats of Some Typical Reactions Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ)
Heat of neutralization	$\text{HCl}(aq) + \text{NaOH}(aq) \longrightarrow \text{NaCl}(aq) + \text{H}_2\text{O}(l)$	-56.2
Heat of ionization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}^+(aq) + \text{OH}^-(aq)$	56.2
Heat of fusion	$\text{H}_2\text{O}(s) \longrightarrow \text{H}_2\text{O}(l)$	6.01
Heat of vaporization	$\text{H}_2\text{O}(l) \longrightarrow \text{H}_2\text{O}(g)$	44.0*
Heat of reaction	$\text{MgCl}_2(s) + 2\text{Na}(l) \longrightarrow 2\text{NaCl}(s) + \text{Mg}(s)$	-180.2

Calculating ΔH_{rxn} Using Known Values: Standard Enthalpies of Formation (ΔH_f°) & Reaction ($\Delta H_{\text{f rxn}}^\circ$)

The standard state of an element: $\Delta H_f^\circ = 0$

- Pure element in its most stable form at 1 atm & 20°C
- Solvents in aqueous solution are at a concentration of 1 M
ex: $\text{H}_2(\text{g})$ $\text{N}_2(\text{g})$ $\text{O}_2(\text{g})$ $\text{Cl}_2(\text{g})$ $\text{Br}_2(\text{l})$ $\text{Hg}(\text{l})$ $\text{Na}(\text{s})$
– all have $\Delta H_f^\circ = 0$

The standard molar enthalpy of formation, ΔH_f°

- ΔH_f for 1 mol substance produced from elements in standard states
- Tabulated for compounds at 1 atm and 20°C
ex: $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H_f^\circ = -393.5 \text{ kJ/mol}$

Calculation of ΔH_{rxn} Using Known Values

Calculating ΔH° of a chemical reaction

- $\Delta H^\circ_{\text{rxn}} = \Delta H_f^\circ \text{ products} - \Delta H_f^\circ \text{ reactants}$
- ex: $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$
- Multiply each ΔH_f° by the stoichiometric coefficient for that species. Ex:

$$\text{C(s)} \quad \Delta H_f^\circ = 1 \times 0\text{kJ/mol} = 0\text{kJ/mol}$$

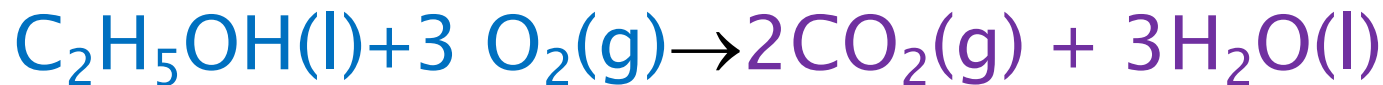
$$\text{O}_2\text{(g)} \quad \Delta H_f^\circ = 1 \times 0\text{kJ/mol} = 0\text{kJ/mol}$$

$$\text{CO}_2\text{(g)} \quad \Delta H_f^\circ = 1 \times -393.5\text{kJ/mol} = -393.5\text{kJ/mol}$$

$$\begin{aligned}\Delta H_{\text{rxn}}^\circ &= \Delta H^\circ_{\text{products}} - \Delta H^\circ_{\text{reactants}} \\ &= -393.5 - (0+0) = -393.5\text{kJ/mol}\end{aligned}$$

*Note: If there are multiple reactants or products, you add the multiple ΔH_f° values before subtracting reactants from products.

Calculate $\Delta H_{\text{rxn}}^\circ$ for the combustion of $\text{C}_2\text{H}_5\text{OH}(\text{l})$
 ΔH_f° values are given below



ΔH_f° Reactants:

$\text{C}_2\text{H}_5\text{OH}(\text{l})$: -277.7 kJ/mol

O_2 : 0 kJ/mol

Total reactants =

ΔH_f° Products

$\text{CO}_2(\text{g})$: -393.5 kJ/mol

$\text{H}_2\text{O}(\text{l})$: -285.8 kJ/mol

Total products =

$\Delta H^\circ = \text{products} - \text{reactants}$

$$A = -1366.7 \text{ kJ}^{25}$$

Hess's Law Of Constant Heat Summation:

Another way to calculate ΔH

The heat of a reaction, ΔH , is constant, whether the reaction is carried out directly in one step or through a number of steps.

The equation for the overall reaction is the sum of two or more other equations (reaction steps).

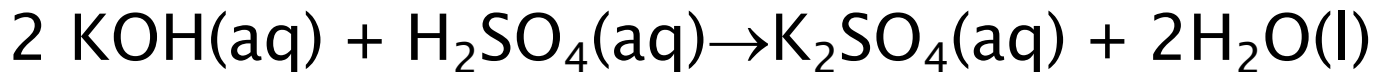
$$\Delta H_{\text{rxn}} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \dots$$

If you reverse a chemical equation, you reverse the sign of ΔH .

$$\Delta H_{\text{forward}} = - \Delta H_{\text{reverse}}$$

Hess' Law Example #1

What is ΔH when KOH(s) reacts with $\text{H}_2\text{SO}_4(\text{aq})$?



This is a 2-step process – dissolve KOH then neutralize –
so need to use Hess' Law

Given information: Styrofoam cup calorimetry was used to determine the following:

Step 1. $\text{KOH(s)} \rightarrow \text{KOH(aq)}$

$$\Delta H_{\text{sol}} \text{ of } \text{KOH(s)} = -58.4 \text{ kJ/mol}$$

Step 2. Neutralization reaction

$$\Delta H \text{ per mole } \text{KOH} = -55.9 \text{ kJ/mol}$$

First: Need **2 mol** KOH in rxn; must double given values.

Then: Add the ΔH s for all steps of the reactions

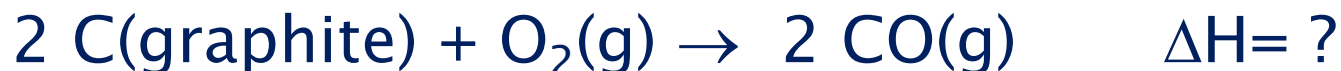
$$A = -228.6 \text{ kJ}^{27}$$

Hess' Law: Using Info From Other Reactions

1. Find each reactant in an equation with known enthalpy
 - Use multiple equations if necessary to find all reactants
2. Find each product in an equation with known enthalpy
 - Use multiple equations if necessary to find all products
3. Add reactions to get the reaction you are looking for
 - Cross out items that are both products & reactants
 - stoichiometry matters, might not cross out all
 - Add multiples
4. Check final equation to make sure it matches the equation of interest.

Hess' Law Example #2

What is the enthalpy of the reaction between carbon and oxygen to form carbon monoxide?



You are given the following reactions with known enthalpies:

