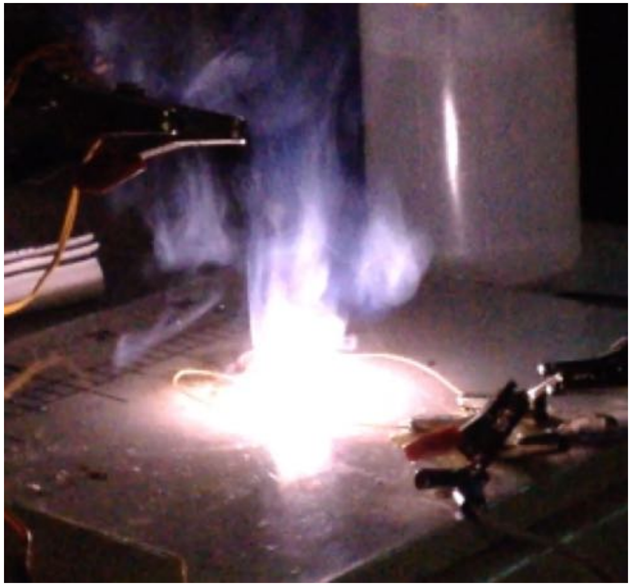
Chapter Six



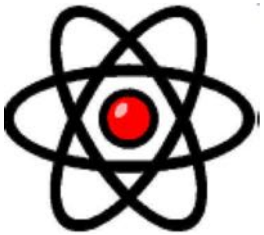
Energy Relationships in Chemical Reactions

Energy (U): Capacity to Do Work

Some types of energy:

Energy = force x distance
= N x m
= kg m^2 / s^2
= kg m^2 s^{-2}

- **Radiant**
  - Energy from the sun
- **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

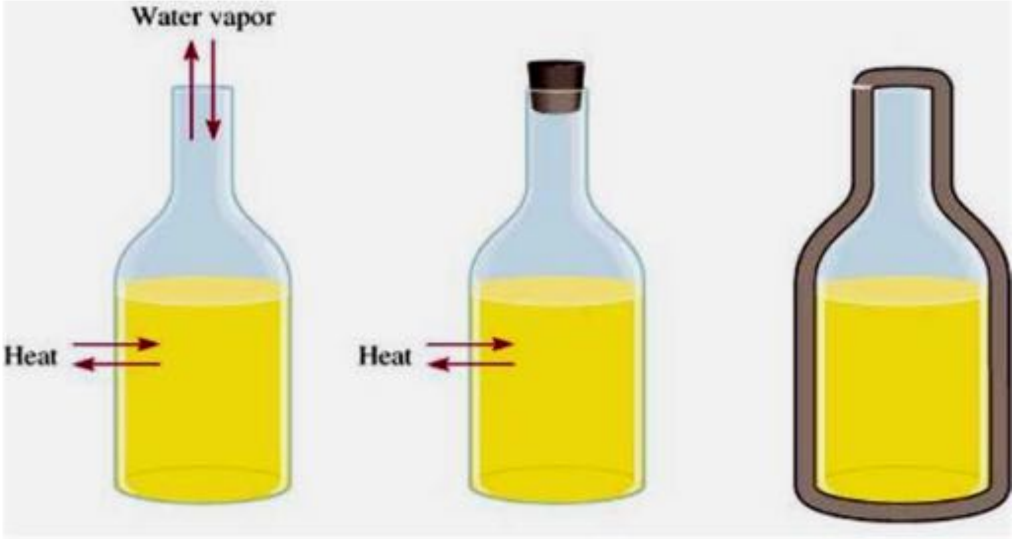
Study of heat change in chemical reactions

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: $CH_4 + O_2 \rightarrow CO_2 + H_2$

Bonds stronger in $CO_2 + H_2O$ than in $CH_4 + O_2$

- 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: H_2O (s) → H_2O (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 of a system:

- Describes specific conditions/macroscopic properties
- Thermo involves measurement of these properties

ex: Potential energy of ball at the top of the mountain

State functions:

Δ = change

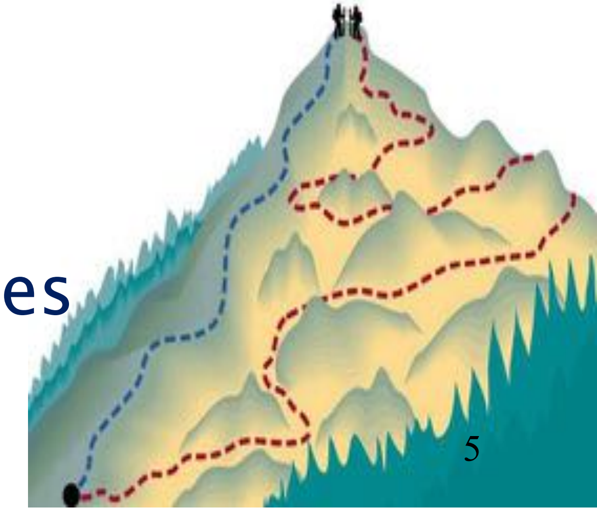
- Properties defined by Δ_{final} - Δ_{initial} values only
  → process doesn't matter
- Composition, temp., pressure, energy, volume

ex: Height of mountain

Path functions:

- Δ_{final} - Δ_{initial} values vary by process
- Heat, work: interdependent variables

ex: # steps taken, Time to top,
energy per step, etc.



First Law of Thermodynamics

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

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

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

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: $\Delta U_{reaction} = U_{products} - U_{reactants}$

Work and Heat

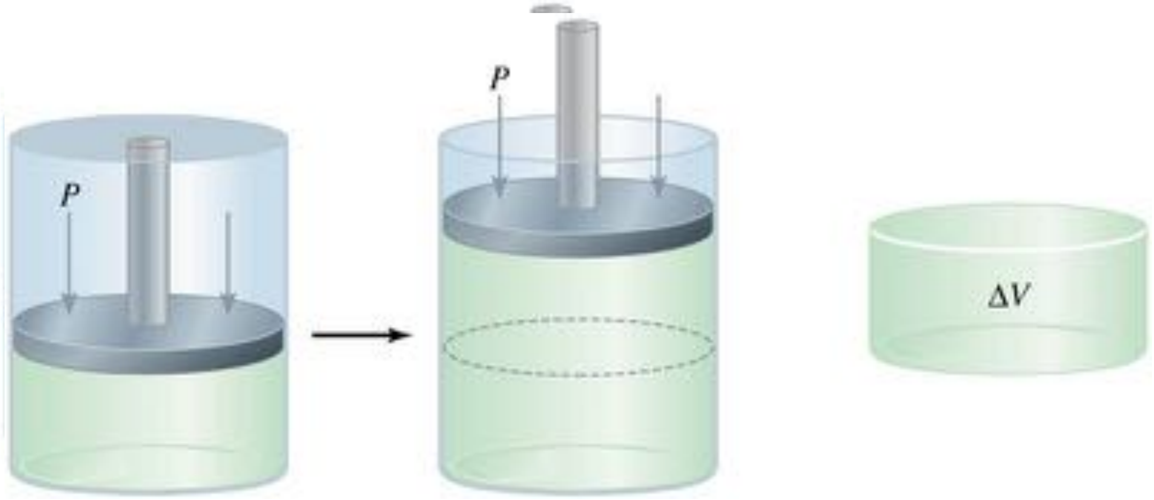
Energy transfer - caused by changes in heat & work in a system

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

Work (w) = force x distance = $-P\Delta V$

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

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



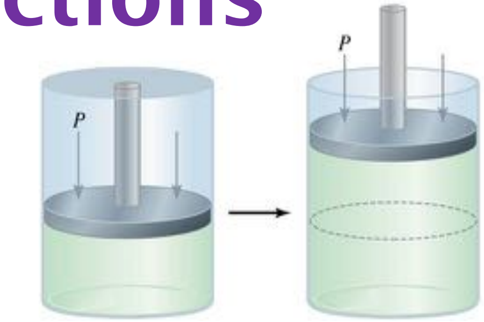
Work (w) = $-P\Delta V$

$\Delta V = V_f - V_i$

For this situation:
$+ \Delta V$
Therefore: -w

1 L x atm = 101.32 J

Work and Heat as Path Functions



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 1atm. (A = 0.000J, -202.6J)

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

b. Calculate the heat required for each system.

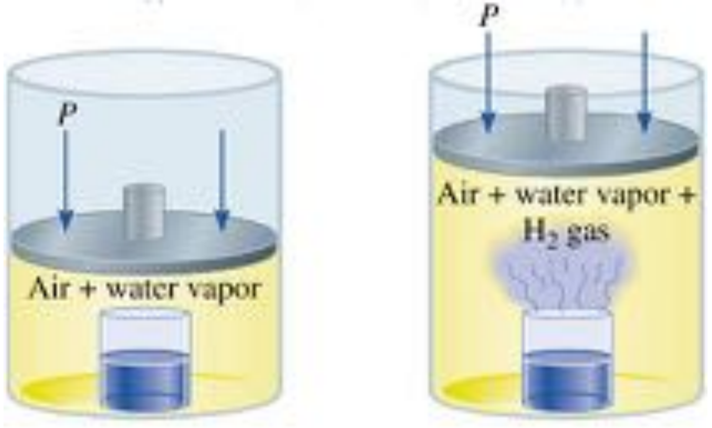
(A = 350.0 J; 552.6 J)

Enthalpy of Chemical Reactions:
Pressure/Volume Relationships with ΔU

For systems at constant pressure (usually ~1atm):

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

w: Takes work to expand system against surroundings.



Enthalpy: (H) Experimentally measured & tabulated

- Can think of as energy of a reaction

At constant pressure: $\Delta H = \Delta U + P\Delta V$

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

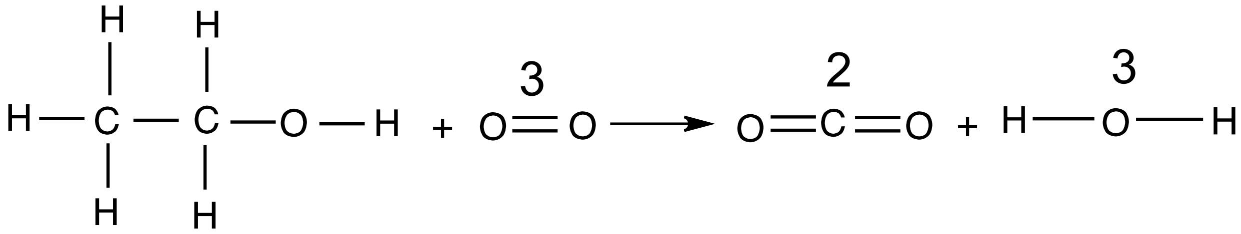
There will be slight differences between ΔH and ΔU

Why is there an enthalpy change during chemical reactions?

(Chapter 9)

Theoretical Calculation: $\Delta H = E_{in} - E_{out}$

$$CH_3CH_2OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$$



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

$\Delta H = E_{in} - E_{out}$
= 1140 kcal/mol – 1380 kcal/mol
= -240 kcal/mol

Real Differences between ΔU and ΔH

(Volume Changes)

ΔH measured experimentally as heat

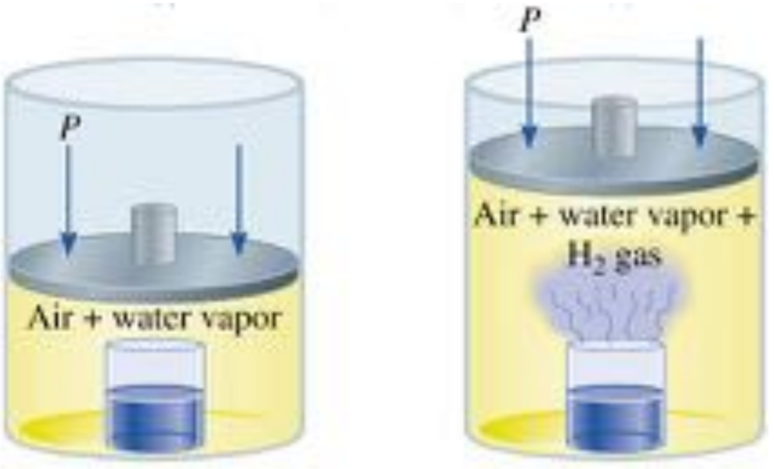
$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$ ΔH=-367.5kJ/mol

Volume change of H_2 gas

V=nRT/P

T= 298K, P=1.0atm, n=1.0mol H_2

V= 24.5L



ΔU = ΔH- P<u>ΔV</u>

ΔH = -367.5kJ

PΔV = 1.0atm x 24.5L = 24.5Latm x 0.101kJ/Latm = 2.5kJ

ΔU = -367.5kJ -2.5kJ= 370kJ

Difference between ΔH and ΔU is only 2.5kJ

~0.7% difference considered negligible

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

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

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

Exothermic Reactions

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

$2SO_2\,(g) + O_2(g) \rightarrow 2SO_3\,(g) + 197.8kJ \qquad \Delta H = -197.8kJ$

Endothermic Reaction

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

$197.8kJ + 2SO_3 \rightarrow 2SO_2\,(g) + O_2(g) \qquad \Delta H = +197.8kJ$

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

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$ $\Delta H = -197.8kJ$

$1SO_2(g) + 1/2O_2(g) \rightarrow 1SO_3(g)$ $\Delta H = -197.8kJ/2 = -98.9kJ$

Note: Write ΔH with units that match mole ratio in equation

$\Delta H = -98.9\ kJ\ /mol\ SO_3(g)$

2. Reverse the reaction, reverse sign of ΔH

$2SO_3 \rightarrow 2SO_2(g) + O_2(g)$ $\Delta H = +197.8kJ$

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 $NO_2(g)$ according to this reaction:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H = -114$ kJ

Info Provided:

Calculate molar mass of NO_2 - convert mass to moles NO_2.

Use coefficient & moles NO_2 present to find ΔH for 15.0 g.

A = +18.6 kJ

Calculating ΔH Via Experiment: Calorimetry

Calorimetry: Measurement of heat changes

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

- $\Delta T = T_{final} - T_{initial}$
- Units: generally °C

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

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

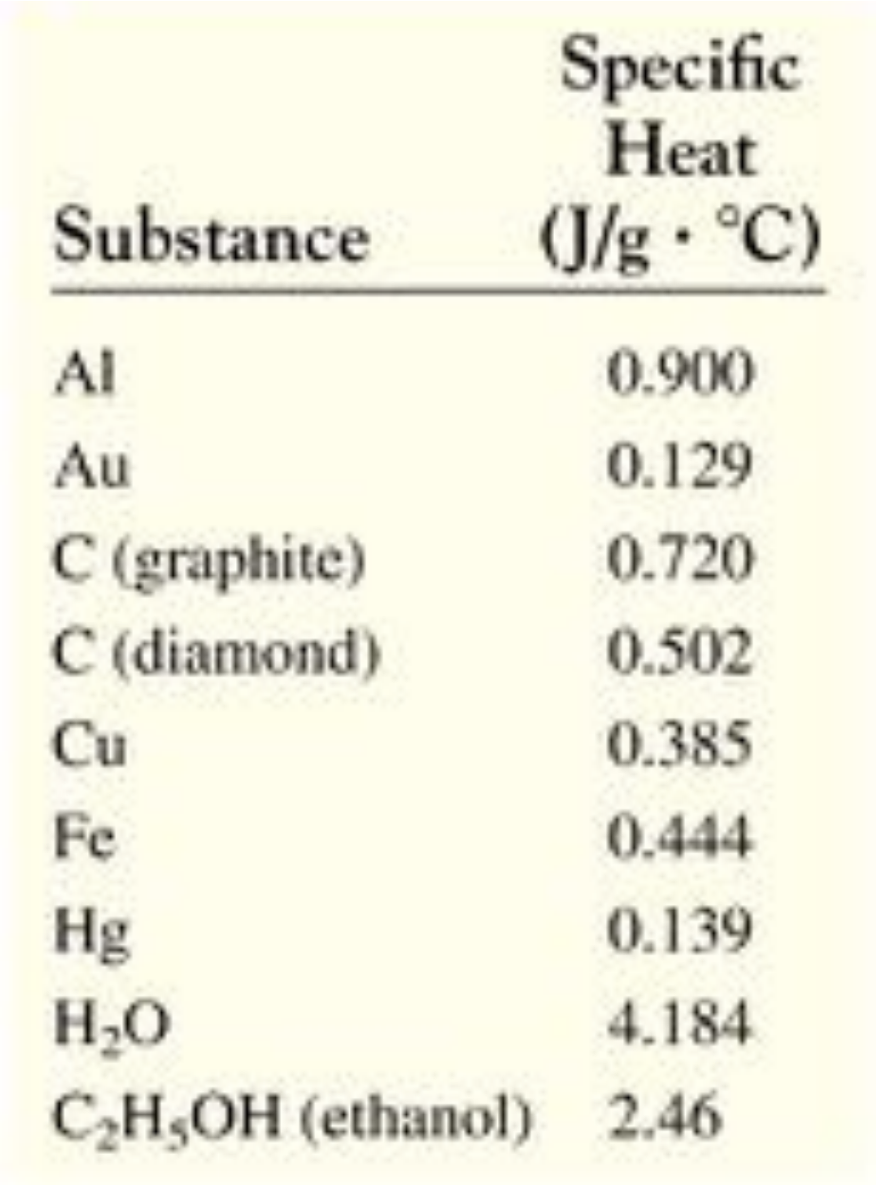
Heat capacity (C): Quantity of heat needed to raise T by 1°C

- $C = m \times s$
- Units: J/°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_2O	4.184
C_2H_5OH (ethanol)	2.46

Calorimetry Experiments

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

$- q_{rxn} = q_{H2O}$

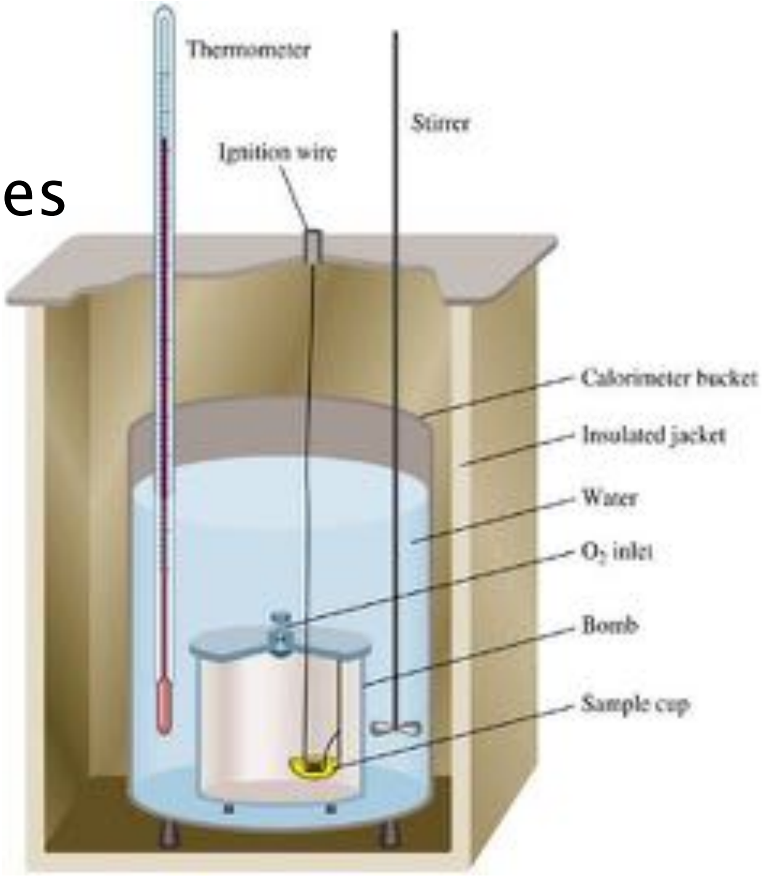
1. Measure ΔT of water

$q_{H2O} = m_{H2O} \times s_{H2O} \times \Delta T_{H2O}$

2. Use q_{H2O} to find system variables

$q_{H2O} = -q_{rxn}$

$q_{rxn} = m_{sys} \times s_{sys} \times \Delta T_{sys}$



Always have 2 sets of variables!

1 for water (surroundings)
1 for reaction (system)

Make 2 columns of variables

Reaction: s, m, $T_{initial}$, T_{final}
Water: s, m, $T_{initial}$, T_{final}

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_{H2O} = 4.18 J/g˚C

What is your equation?

What info is provided?

Solve for q_{H2O} ($q_{H2O} = -q_{metal}$)

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

A = 0.269 J/g˚C

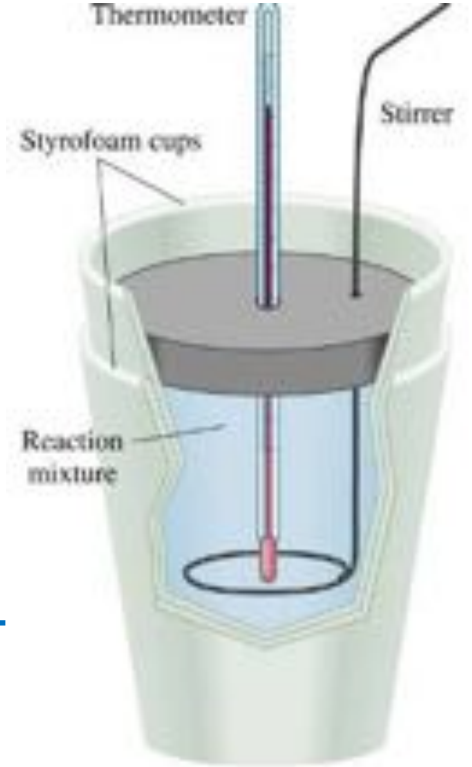
Heat Evolved During a Chemical Reaction

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 ($-q_{rxn}$)

Two solutions are mixed in the calorimeter

40.0 mL of 1.00 M KOH(aq)
40.0mL of 0.500M H_2SO_4(aq)
T_i of both solutions = 21.00°C



Data on final solution

Density:	1.02 g/mL	Volume:	80.0 mL
S.H.:	4.00 J/g°C	Temp.:	27.85°C

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

1. What is the chemical reaction?

$$2\ KOH + H_2SO_4 \rightarrow K_2SO_4(aq) + 2H_2O$$

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

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

2. What information is given?

Initial Information:	Final information:
40.0 mL of 1.00 M KOH(aq)	Density: 1.02 g/mL
40.0 mL of 1.00 M H_2S0_4(aq)	Volume: 80.0 mL
T_i of both solutions = 21.00°C	S.H.: 4.00 J/g°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 81.6g of reactants, 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_{H2O} 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 $q_{H20} = -q_{rxn}$.

A = -55.9 kJ/mol

Typical Heats of Reactions

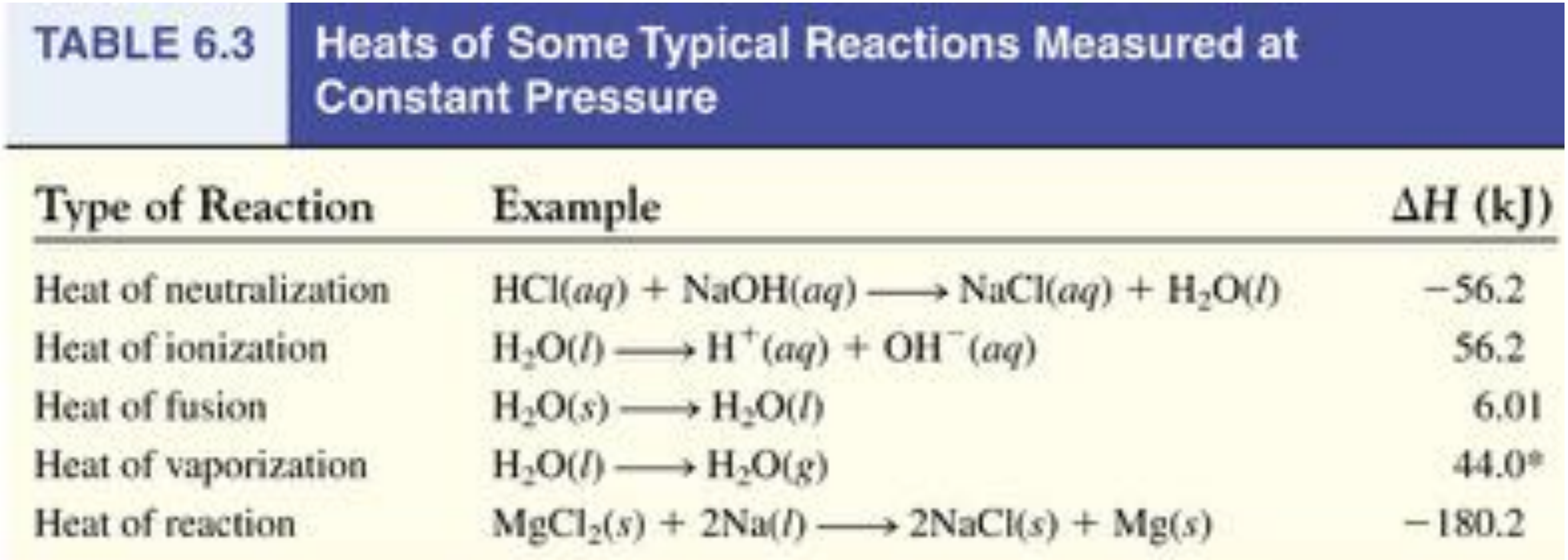


TABLE 6.3 Heats of Some Typical Reactions Measured at Constant Pressure

Type of Reaction	Example	ΔH (kJ)
Heat of neutralization	$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$	−56.2
Heat of ionization	$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq)$	56.2
Heat of fusion	$H_2O(s) \longrightarrow H_2O(l)$	6.01
Heat of vaporization	$H_2O(l) \longrightarrow H_2O(g)$	44.0*
Heat of reaction	$MgCl_2(s) + 2Na(l) \longrightarrow 2NaCl(s) + Mg(s)$	−180.2

Calculating ΔH_{rxn} Using Known Values: Standard Enthalpies of Formation ($\Delta H_f°$) & Reaction ($\Delta H_f°_{rxn}$)

The standard state of an element: **$\Delta H_f° = 0$**

- Pure element in its most stable form at 1 atm & 20°C
- Solvents in aqueous solution are at a concentration of 1 M

ex: $H_2(g)$ $N_2(g)$ $O_2(g)$ $Cl_2(g)$ $Br_2(l)$ $Hg(l)$ $Na(s)$

– all have $\Delta H_f° = 0$

The standard molar enthalpy of formation, $\Delta H_f°$

- ΔH_f for 1 mol substance produced from elements in standard states
- Tabulated for compounds at 1atm and 20°C

ex: $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_f° = -393.5 kJ/mol$

Calculation of ΔH_{rxn} Using Known Values

Calculating ΔH° of a chemical reaction

- **$\Delta H^\circ_{rxn} = \Delta H_f^\circ$ products - ΔH_f° reactants**
- **ex: $C(s) + O_2(g) \rightarrow CO_2(g)$**
- Multiply each ΔH_f° by the stoichiometric coefficient for that species. Ex:

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

$O_2(g)$ $\Delta H_f^\circ = 1 \times 0 kJ/mol = 0 kJ/mol$

$CO_2(g)$ $\Delta H_f^\circ = 1 \times -393.5 kJ/mol = -393.5 kJ/mol$

$$\Delta H_{rxn}^\circ = \Delta H^\circ_{products} - \Delta H^\circ_{reactants}$$

$$= -393.5 - (0+0) = -393.5 kJ/mol$$

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

Calculate ΔH_{rxn}° for the combustion of $C_2H_5OH(l)$ ΔH_f° values are given below

$C_2H_5OH(l) + 3\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

ΔH_f° Reactants:

C_2H_5OH (l): -277.7 kJ/mol

O_2: 0 kJ/mol

Total reactants =

ΔH_f° Products

$CO_2(g)$: -393.5 kJ/mol

$H_2O(l)$: -285.8 kJ/mol

Total products =

ΔH° = products - reactants

A = -1366.7 kJ

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).

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

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

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

Hess' Law Example #1

What is ΔH when KOH(s) reacts with H_2SO_4 (aq)?

2 KOH(aq) + H_2SO_4(aq) → K_2SO_4(aq) + $2H_2O$(l)

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. KOH(s) → KOH(aq)

ΔH_{sol} of KOH(s) = -58.4 kJ/mol

Step 2. Neutralization reaction

ΔH per mole KOH = –55.9 kJ/mol

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

Then: Add the ΔHs for all steps of the reactions

A = -228.6 kJ

Hess' Law: Using Info From Other Reactions

1. Find each reactant in 1 equation only
   - Use multiple equations if necessary to find all reactants

2. Find each product in 1 equation only
   - Use multiple equations if necessary to find all products

3. Add reactions
   - Cross out items that are both products & reactants
     - stoichiometry matters, might not cross out all
   - Add multiples

4. Check final equation

Hess' Law Example #2

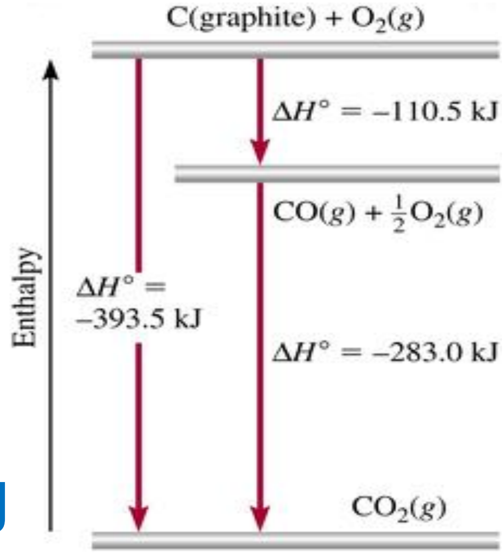
What is the enthalpy of the reaction between carbon and oxygen to form carbon dioxide?

2 C(graphite) + O_2(g) → 2 CO(g) ΔH= ?

You are given the following information:

C(graphite) + O_2(g) → CO_2(g) ΔH = -393.5 kJ

2 CO(g) + O_2(g) → 2 CO_2(g) ΔH = -566.0 kJ



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2 C(graphite) + O_2(g) → 2 CO(g) ΔH= -221.0 kJ