

Chemistry 2

Thermodynamics : the study of energy and its transformations

Thermochemistry : the relationship between chemical reactions and energy changes involving heat.

Energy = the capacity to do work or produce heat

→ SI unit: joule (J) -

The Nature of Energy

→ Potential energy (due to objects position)

- gravitational energy: due to height / force of gravity
- electrostatic energy: separation of charges cation (+) and anion (-)
- chemical potential energy: energy stored in chemical bonds

→ Kinetic energy (due to objects motion / velocity)

$$KE = \frac{1}{2}mv^2$$

• Thermal KE: due to samples temperature

$$\hookrightarrow \text{Reminder: } (KE)_{\text{avg}} = \frac{3}{2}kT \text{ (only influenced by temp)}$$

Systems

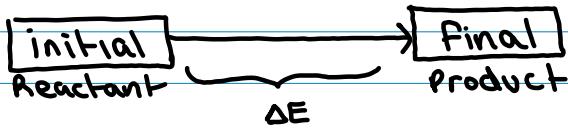
- system: part of universe on which we are studying the energy change
- surrounding: everything else in the universe
- universe: system + surroundings

Types of Systems

- Open = matter and energy exchanged with surroundings
- Closed = only energy exchanged with surroundings
- Isolated = no matter or energy exchanged with surroundings

Internal energy (E)

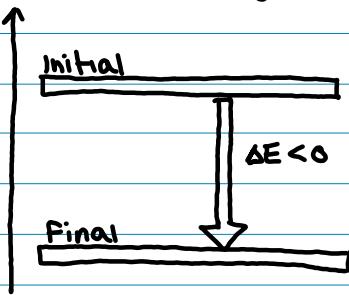
- sum of all potential and kinetic energies of all the components (atoms, molecules, ions in the system)
- Numerical value of E is unknown and cannot be calculated
- * We CAN measure the change in internal energy (ΔE)



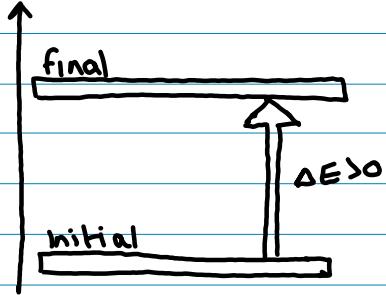
$$\Delta E = E_{\text{final}} - E_{\text{initial}} \quad / \quad \Delta E = E_{\text{product}} - E_{\text{reactant}}$$

Energy diagrams:

Loss in energy (ΔE neg.)



Gain in energy (ΔE pos.)



Law of conservation of energy (1st law thermodyn.)

→ energy cannot be created nor destroyed

→ It can be transferred or transformed (different forms)

The total energy of the universe is constant

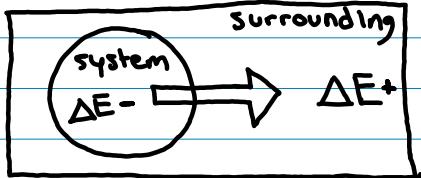
$$\Delta E_{\text{universe}} = 0$$

$$\Delta E_{\text{universe}} = \Delta E_{\text{system}} + \Delta E_{\text{surrounding}} = 0 \quad (\text{by def.})$$

- Whatever the system gains or loses will be lost or gained by its surroundings
- The system can gain or lose energy through exchange with its surrounding
- * When energy gets transferred or converted, the total amount of energy present at the beginning must be present at the end.

Energy Flow

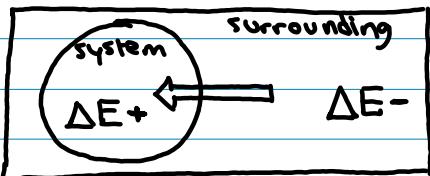
- When energy flows out of system (ΔE_{sys} neg (-))
 → It must all flow into the surrounding (ΔE_{surr} pos (+))



$$-\Delta E_{\text{sys}} = \Delta E_{\text{surr}}$$

$(E \text{ loss})$ $(E \text{ gain})$

- When energy flows into the system (ΔE_{sys} pos (+))
 → It must all come from the surrounding (ΔE_{surr} neg (-))

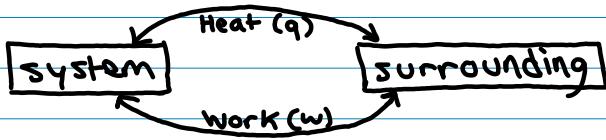


$$\Delta E_{\text{sys}} = -\Delta E_{\text{surr}}$$

$(E \text{ gain}) \quad (E \text{ loss})$

Energy Exchange

energy is exchanged between the system and the surroundings through either heat or work



Work (w) = energy to cause an object with mass to move against a force
= energy transferred when a force moves an object

$$w = F \times d$$

w = work (J)

F = force (N)

d = distance (m)

Heat (q) = energy transferred from a hotter object to a colder one (due to temp. difference)

q = heat (J)

$$\Delta E = q + w$$

ΔE = internal energy change for system (J)

q = energy transferred as heat between sys. and surr. (J)

w = energy transferred as work between sys. and surr. (J)

Thermodynamic quantities : 1) Number + unit = magnitude
2) Sign = direction of change

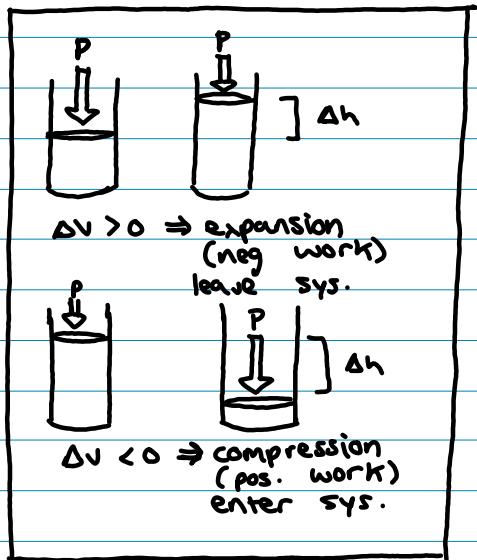
Sign	(+)	(-)
ΔE	Net gain of energy by sys	Net loss of energy by sys
q	Sys. gains heat (endothermic)	Syst. loses heat (exothermic)
w	work done on system by surrounding (enter the system - inward)	work done by system on surrounding (exit the system - outward)

Pressure - Volume Work (PV)

→ Type of work associated with chemical processes:

- work done by an ideal gas (expansion) - neg.
- work done to an ideal gas (compression) - pos.

$$W = -P \Delta V$$



W: work (J)
P: external pressure (kPa)
 ΔV : volume change (L)

units:
 $kPa \times L = J$
 $atm \times \frac{101.3 \text{ kPa}}{atm} \times L = J$

* convert to
kPa for J

$$\begin{aligned} W &= F \times d \\ &= F \times \Delta h \\ &= \underbrace{P \times A}_{P = \frac{F}{A}} \times \Delta h \\ &= P \times \Delta V \\ W &= -P \cdot \Delta V \end{aligned}$$

ex: Hot air balloon heating ~~expands~~ the air inside to inflate.
 Volume changes from $4.00 \times 10^6 \text{ L}$ to $4.50 \times 10^6 \text{ L}$ by
 the addition of $1.3 \times 10^8 \text{ J}$ of energy. Assume balloon
 expands against constant pressure of 1.0 atm.
 Calculate ΔE .

$$\begin{aligned} \Delta E &= q + w \\ &= (1.3 \times 10^8 \text{ J}) + (-1 \text{ atm} \cdot \frac{101.3 \text{ kPa}}{\text{atm}} (4.50 \times 10^6 - 4.00 \times 10^6)) \\ &= (1.3 \times 10^8) + (-5.1 \times 10^7) \\ &= \boxed{7.9 \times 10^7 \text{ J}} \end{aligned}$$

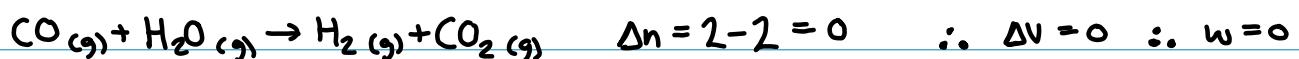
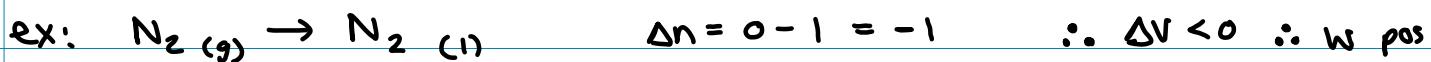
Predicting the sign of work for a reaction from a balanced equation

- 1) Only gases can do PV work
- 2) Ignore solid, liquid, aqueous
- 3) Consider gases behaving ideally at constant pressure and temperature

$$\boxed{P\Delta V = \Delta n RT}$$

Δn : number of moles of gaseous products
- number of moles of gaseous reactants
(From coefficient of balanced equation)

- $\Delta n > 0 \Rightarrow$ reaction will expand in volume ($\Delta V > 0$)
 $\therefore w$ neg (-) - w by sys to surr
- $\Delta n < 0 \Rightarrow$ reaction will compress in volume ($\Delta V < 0$)
 $\therefore w$ pos (+) - w by surr on sys



Heat (q)

- exchange of thermal energy between sys and surr
- occurs when sys and surr have different temp
(go from high temp → low temp)
 - Temperature = measures the motion (degree of agitation) of cold and hot

When a sys. absorbs heat → temp increases
(directly proportional)

- The proportionality constant is called heat capacity (C).
 - ⇒ system's ability to absorb thermal energy without undergoing a large temp. change.

When an object is heated / cooled, the amount of energy depends on:

- The identity of the material
- The quantity of material
- The magnitude of temperature change

Specific heat capacity (C_s)

- energy required to raise the temp. of one gram of a substance by 1°C

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

C_s : ($\text{J/g}\cdot\text{C}$)
 q : energy transferred (J)
 m : mass (g)
 ΔT : $T_f - T_i$ ($^\circ\text{C}$ or K)

Molar heat capacity (C_m)

- energy required to raise the temp. of one mole of a substance by 1°C

$$C_m = \frac{q}{n \Delta T}$$

n : moles of substance (mol)

H_2O specific heat capacity ($4.18 \text{ J/g}^\circ\text{C}$)

→ The high heat capacity allows water to absorb a large amount of energy (heat) without a large temp. increase.

- The large amount of water absorbing heat from the air keeps beaches cool
 - without water, the earth's average temp. would be 107°C vs 14°C (what it is now).
- Water is commonly used as a coolant because it can absorb a lot of heat and remove it from the important mechanical parts to keep them from overheating.

Quantifying Heat energy transfer

$$q = (m) \times (c_s) \times (\Delta T)$$

or

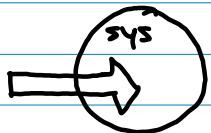
$$q = (n) \times (C_m) \times (\Delta T)$$

$$q = m C \Delta T$$

Endothermic and Exothermic Processes

Endothermic
($q_{sys} > 0$)

Heat flows into
sys. from surr



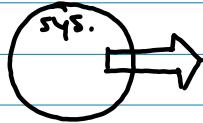
sys. gains
energy
(q pos.)

ex: process of melting ice

vs

Exothermic
($q_{sys} < 0$)

Heat flows out of
sys. to surr



sys loses
energy
(q neg.)

ex: a rxn that produces
heat

Endothermic and Exothermic Reactions

- Chemical Heat pack - exothermic reaction
⇒ hands get warm b/c the released heat of the reaction is transferred to your hands.



- Chemical Cold pack - endothermic reaction (dissolution)
⇒ hands get cold because the pack is absorbing your heat to let the reaction take place.



Thermal Energy Transfer

- When 2 substances of different temperature are combined, thermal energy flows from the hotter substance to the cooler one until both reach the same temperature.
- ⇒ Thermal equilibrium = once both substances have reached the same temperature

If we assume that the 2 substances are thermally isolated from everything else, then the heat lost by one substance exactly equals the heat gained by the other (First Law of thermodynamics).

$$q_1 = -q_2$$

ex. A 55.0g piece of metal whose temp. is 99.8°C is placed in a beaker containing 225g of H_2O at 21.0°C . $T_f = 23.1^{\circ}\text{C}$. What is the specific heat capacity of the metal?
($C_{\text{H}_2\text{O}} = 4.18 \frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}}$)

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

$$m_{\text{H}_2\text{O}} \cdot C_{\text{H}_2\text{O}} \cdot \Delta T_{\text{H}_2\text{O}} = - m_{\text{metal}} \cdot C_{\text{metal}} \cdot \Delta T_{\text{metal}}$$
$$(225\text{g})(4.18 \frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}})(23.1^{\circ}\text{C} - 21.0^{\circ}\text{C}) = -(55.0\text{g}) \cdot C_{\text{metal}} \cdot (23.1^{\circ}\text{C} - 99.8^{\circ}\text{C})$$

$$C_{\text{metal}} = 0.47 \frac{\text{J}}{\text{g}\cdot^{\circ}\text{C}}$$

Enthalpy (H)

→ A thermodynamic function that accounts for heat flow in processes occurring at constant pressure.

Enthalpy Change (ΔH)

→ Quantity of thermal energy change of a system at constant pressure.

$$\Delta H = q_p \quad \text{constant pressure}$$

ΔH considers thermal energy

ΔE considers both thermal energy and work

Def:

$$\boxed{\Delta H = \Delta E + P\Delta V}$$

$$\Delta E = q_p + w$$

$$\Delta E = (\Delta H) + (-P\Delta V)$$

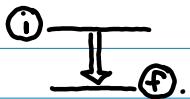
$$\Delta H = \Delta E + P\Delta V$$

Enthalpies of Reaction (ΔH_{rxn})

$$\boxed{\Delta H_{rxn} = H_{product} - H_{reactant}}$$

$$\Delta H_{rxn} < 0$$

$\therefore H_{product} < H_{reactant}$
exothermic (loss H)

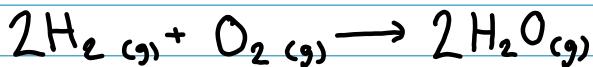


$$\Delta H_{rxn} > 0$$

$\therefore H_{product} > H_{reactant}$
endothermic (gain)



Ex: thermochemical equation



$\Delta H = -486.3 \text{ kJ}$ per mol
of rxn

i.e. per 2 mol H_2 ,
1 mol O_2 , 2 mol H_2O

ΔH vs ΔE

- $\Delta H = \Delta E$, if no change in volume occurs ($\Delta V = 0 \Rightarrow \text{no work}$)
- In rxns that produce / consume large amounts of gas (large ΔV), $\Delta H \neq \Delta E$

ex: the reaction at 25°C of sodium metal in water carried out in a beaker open to the atmosphere at 1.00 atm is:



Convert from ΔH to ΔE

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

$$\Delta E = \Delta H - \underbrace{P\Delta V}_{\text{use } 1}$$

$$= \Delta H - \Delta n RT$$

$$\Delta n = 1 - 0 = 1$$

$$\left. \begin{array}{l} \textcircled{1} R = 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}} \\ \textcircled{2} R = 0.08206 \frac{\text{atm} \cdot \text{L}}{\text{K} \cdot \text{mol}} \end{array} \right\} \begin{array}{l} \text{use } \textcircled{1} \\ \text{for J} \end{array}$$

$$\begin{aligned} \Delta E &= (-386.6 \times 10^3 \text{ J}) - (1 \text{ mol})(8.314)(298 \text{ K}) \\ &= -371.1 \times 10^3 \text{ J} \end{aligned}$$

$$\therefore \Delta H = -386.6 \text{ kJ}$$

$$\Delta E = -371.1 \text{ kJ}$$

* It makes sense that more energy is lost in ΔE b/c $\Delta n > 0$

$$\therefore \Delta V > 0$$

$$\therefore w < 0$$

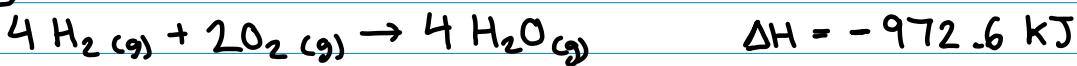
Characteristics of Enthalpy Change

→ Enthalpy is an extensive property (related to amount of substance). The magnitude of ΔH is directly proportional to the quantities of reactants and products in a reaction.

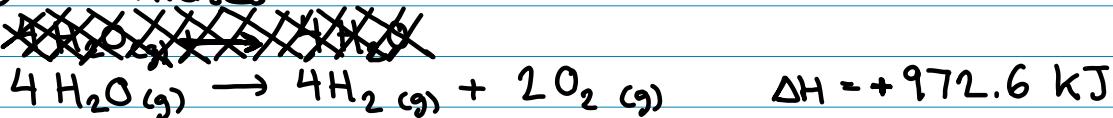


- ① If the coefficients in a balanced equation are multiplied by a factor, the value of ΔH is multiplied by the same factor.
- ② If a reaction is reversed, the sign of ΔH is also reversed.
- ③ Enthalpy change for a reaction depends on the state of the reactants and products.

ex.: ① $\times 2$



ex.: ① $\times 2$ inverted

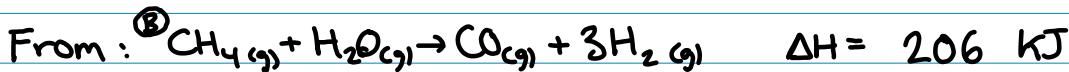


$$\Delta H_{\text{vap}} = 40.7 \text{ kJ}$$



$$\Delta H \neq 972.6 \text{ kJ}$$

b/c diff. state



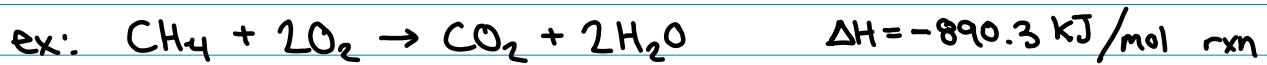
Which is more exothermic (rank)

- a. $2\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{CO} + 6\text{H}_2 \quad \text{④} \times 2 \therefore \Delta H = 412 \text{ kJ}$
- b. $2\text{CO} + 6\text{H}_2 \rightarrow 2\text{CH}_4 + 2\text{H}_2\text{O} \quad \text{⑤} \times 2 \text{ reverse} \therefore \Delta H = -412 \text{ kJ}$
- c. $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \text{⑥} \text{ reverse} \therefore \Delta H = -206 \text{ kJ}$

b - c - a

Stoichiometry in Heat of Reaction

→ Quantity of heat obtained depends on the amount of reactants



How much heat is obtained from 10.0 g methane (assume excess oxygen)?

$$10.0 \text{ g CH}_4 \cdot \frac{\text{mol CH}_4}{16.04 \text{ g CH}_4} \cdot \frac{-890.3 \text{ kJ}}{1 \text{ mol CH}_4} = -555 \text{ kJ}$$

Determine Enthalpy of Reaction (ΔH_{rxn})

→ Measure by calorimetry

- calorimetry = measurement of heat flow by determining the temp. change produced by the heat flow.
- calorimeter = apparatus used to determine experimentally the heat associated with a chemical reaction.
 - constant pressure (coffee-cup)
 - constant volume (bomb)

Constant pressure calorimeter (coffee-cup)

- For reactions that occur in solution

→ Constant pressure: $q_p = \Delta H$

How it works:

1st scenario: (isolated system) heat transfers ONLY between reaction and soln

$$\Delta T_{soln} > 0$$

$$q_{soln} = -q_{rxn} \text{ (loss)}$$

$$\Delta T_{soln} < 0$$

$$-q_{soln} = q_{rxn} \text{ (gain)}$$

2nd scenario: heat transfer occurs between calorimeter, soln', rxn

$$\Delta T_{soln} > 0$$

$$q_{soln} + q_{cal} = -q_{rxn} \text{ (loss)}$$

$$\Delta T_{soln} < 0$$

$$-(q_{soln} + q_{cal}) = q_{rxn} \text{ (gain)}$$

* $C_{cal} = \frac{q_{cal}}{\Delta T}$ $\Rightarrow q_{cal} = C_{cal} \cdot \Delta T$

- no mass, it's for the entire calorimeter (J/°C)
- calorimeter constant (C_{cal}) is the amount of heat absorbed by the calorimeter for each 1°C increase.

ex: 0.05g of Mg chips are placed in a coffee-cup cal. and 100.0mL of 1.00 M HCl is added. The temp. increases from 295.36 K to 297.61 K. What is the enthalpy change of the rxn per mole of Mg? (C_s of soln = 4.20 J/g.K, density HCl soln = 1 g/mL)



$$q_{\text{soln}} = -q_{\text{rxn}}$$

$$\underbrace{m_{\text{soln}} \cdot C_s \cdot \Delta T_{\text{soln}}}_{* m_{\text{soln}} = (m_{\text{HCl soln}} + m_{\text{Mg}})} = -q_{\text{rxn}}$$

$$(0.05\text{g} + 100\text{mL} \cdot \frac{1\text{g}}{1\text{mL}})(4.20)(297.61 - 295.36) = -q_{\text{rxn}}$$

$$q_{\text{rxn}} = -945.47 \text{ J}$$

$$\frac{-945.47 \text{ J}}{0.05 \text{ g Mg}} \cdot \frac{24.31 \text{ g Mg}}{\text{mol Mg}} = -460 \text{ kJ/mol Mg}$$

ex: Add 50mL of water at 55.2°C to calorimeter containing 50mL of water at 23.5°C. Final temp. of the sys is 37.6°C. Calculate the heat ~~capacity~~ capacity of the calorimeter. (C_s of water = 4.18 J/g°C, density of water = 1 g/mL)
 * Calorimeter initial temp. (T_i) = same as whatever is initially inside.

$$-\frac{\text{energy loss}}{q_{\text{hot}}} = \frac{\text{gain}}{(q_{\text{cold}} + q_{\text{cal}})}$$

$$-m_{\text{hot}} \cdot C_{\text{H}_2\text{O}} \cdot \Delta T_{\text{hot}} = m_{\text{cold}} \cdot C_{\text{H}_2\text{O}} \cdot \Delta T_{\text{cold}} + C_{\text{cal}} \cdot \Delta T_{\text{cold}}$$

$$-(50\text{g})(4.18)(37.6 - 55.2) = (50\text{g})(4.18)(37.6 - 23.5) + C_{\text{cal}}(37.6 - 23.5)$$

$$-3681.92 \text{ J} = 2949.72 \text{ J} + C_{\text{cal}}(14.1)$$

$$\frac{-3681.92 \text{ J}}{14.1 \text{ °C}} = C_{\text{cal}}$$

$$C_{\text{cal}} = 51.9 \text{ J/°C}$$

* no mass (g)

Constant volume calorimeter (bomb)

- combustion reactions (in bomb) $\Rightarrow \Delta E_{\text{comb}}$

\hookrightarrow exothermic (absorbed by H_2O)

\rightarrow constant volume:

$$q_v = \Delta E$$

$$\Delta E = q + vT^{\circ} \frac{b/c}{\cancel{\Delta V = 0}}$$
$$\Delta E = q_v$$

* NOT ΔH b/c $\Delta H = q_p$ (pressure must be constant)

How it works:

1st scenario: $C_{\text{cal}} =$ heat absorbed by bomb and water as a whole

2nd scenario: $C_{\text{bomb}} + C_{\text{water}}$

* Once we find ΔE , we can proceed to find ΔH by using the relationship'

$$\boxed{\Delta H = \Delta E + P\Delta V}$$

At this point, we are not considering ΔV to be 0.

The constant volume was just in the calorimeter which was a tool to find ΔE .

\rightarrow we can say $P\Delta V = \Delta nRT$

so with the balanced equation (coefficients of gases) and a temperature, we can find ΔH .

ex: combustion of CH_6N_2 with O_2 produces N_2 , CO_2 , H_2O .

4.00g of CH_6N_2 is combusted in a bomb calorimeter, the temp of the calorimeter increases from 25°C to 39.5°C .

Calculate energy of combustion per mole of CH_6N_2 if $C_{\text{cal}} = 7.794 \text{ kJ}/\text{C}$.



$$-\dot{q}_{\text{rxn}} = q_{\text{cal}}$$

$$= C_{\text{cal}} \cdot \Delta T_{\text{cal}}$$

$$= (7794 \text{ kJ}/\text{C})(39.5 - 25)$$

$$-\dot{q}_{\text{rxn}} = 113 \text{ kJ}$$

$$\boxed{\dot{q}_{\text{rxn}} = -113 \text{ kJ}} \Rightarrow \text{for } 4\text{g}$$

$$\frac{-113 \text{ kJ}}{4\text{g}} \cdot \frac{46.07 \text{ g}}{\text{mol}} = \boxed{-1.3 \times 10^3 \text{ kJ/mol } \text{CH}_6\text{N}_2 = \Delta E}$$

ex: $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}$

1.00g glucose is burned in a calorimeter (bomb-constant v).

Bomb is in insulating container with 1.2 kg of water. Temp. of water and bomb rise from 25°C to 33.2°C . What is the energy of combustion per mole of glucose?

($C_{\text{bomb}} = 837 \text{ J}/\text{C}$, $C_{\text{water}} = 418 \text{ J/g}^\circ\text{C}$)

$$-\dot{q}_{\text{rxn}} = q_{\text{bomb}} + q_{\text{water}}$$

$$-\dot{q}_{\text{rxn}} = C_{\text{bomb}} \cdot \Delta T + m_{\text{water}} \cdot C_{\text{water}} \cdot \Delta T$$

$$-\dot{q}_{\text{rxn}} = (837 \text{ J}/\text{C})(33.2 - 25) + (1.2 \times 10^3 \text{ g})(418)(33.2 - 25)$$

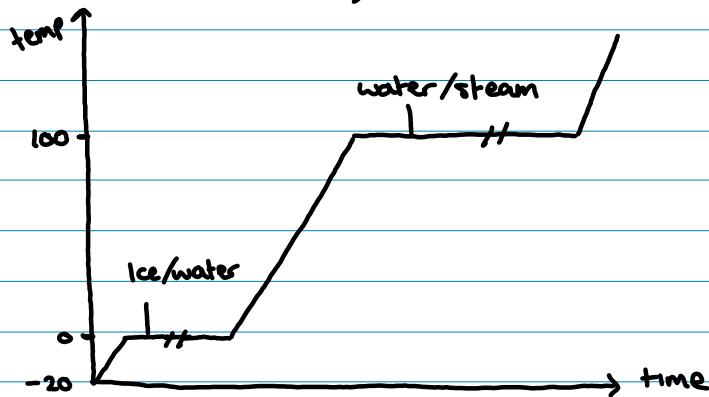
$$\dot{q}_{\text{rxn}} = -48.1 \times 10^3 \text{ J}/1.00 \text{ g glucose}$$

$$\frac{-48.1 \times 10^3 \text{ J}}{1.00 \text{ g}} \cdot \frac{180,156 \text{ g}}{\text{mol}} = \boxed{-8.67 \times 10^6 \text{ J/mol}} = \Delta E$$

Energy and changes of state

- Any change of state involves the addition /removal of energy as heat.
- Heat of fusion (ΔH_{fus}) = energy transferred as heat that is required to convert a solid, at its melting point, to liquid (kJ/mol or J/g)
- Heat of vaporization (ΔH_{vap}) = energy transferred as heat that is required to convert a liquid, at its boiling point, to vapor (kJ/mol or J/g)

ex: H_2O (heating curve)



Fusion:



$$\Delta H_{fus} = 6.01 \text{ kJ/mol}$$

Vaporization:



$$\Delta H_{vap} = 40.7 \text{ kJ/mol}$$

ex: Calculate the energy needed to convert 500g of ice at -50°C to vapor at 200°C .

$$(\Delta H_{\text{fus}} = 333 \text{ J/g}, \Delta H_{\text{vap}} = 2256 \text{ J/g}) \quad \cancel{\text{Cs}}$$

$$(C_s \text{ H}_2\text{O}_{(s)} = 2.06 \text{ J/gK}, C_s \text{ H}_2\text{O}_{(l)} = 4.18 \text{ J/gK}, C_s \text{ H}_2\text{O}_{(g)} = 1.86 \text{ J/gK})$$

Total Heat

- $q_1 \Rightarrow$ ice -50°C to 0°C
- $q_2 \Rightarrow$ at 0°C ΔH_{fus}
- $q_3 \Rightarrow$ liquid 0°C to 100°C
- $q_4 \Rightarrow$ at 100°C ΔH_{vap}
- $q_5 \Rightarrow$ gas 100°C to 200°C

$$\begin{aligned} q_1 &= m_{\text{ice}} C_{\text{ice}} \Delta T = (500)(2.06)(0 - (-50)) = 5.15 \times 10^4 \text{ J} \\ q_2 &= m \cdot \Delta H_{\text{fus}} = (500)(333 \text{ J/g}) = 1.67 \times 10^5 \text{ J} \\ q_3 &= m_{\text{liq}} \cdot C_{\text{liq}} \cdot \Delta T = (500)(4.18)(100 - 0) = 2.09 \times 10^5 \text{ J} \\ q_4 &= m \cdot \Delta H_{\text{vap}} = (500)(2256 \text{ J/g}) = 1.13 \times 10^6 \text{ J} \\ q_5 &= m_{\text{gas}} C_{\text{gas}} \Delta T = (500)(1.86)(200 - 100) = 9.3 \times 10^4 \text{ J} \end{aligned}$$

$$\boxed{q_{\text{total}} = 1.65 \times 10^6 \text{ J} = 1.65 \times 10^3 \text{ KJ}}$$

ex: Ice cube problem

What is the minimum amount of ice at 0°C that must be added to a can of cola (340 mL) to cool the cola from 20.5°C to 0°C .

$$(\Delta H_{\text{fus H}_2\text{O}} = 333 \text{ J/g}, C_s \text{ cola} = 4.18 \text{ J/g°C}, \text{cola density } 1 \text{ g/mL})$$

energy loss energy gain

$$-q_{\text{cola}} = q_{\text{ice}} \quad (\text{at } 0^{\circ}\text{C} - \text{at plateau})$$

$$-m_{\text{cola}} C_{\text{cola}} \Delta T_{\text{cola}} = m_{\text{ice}} \cdot \Delta H_{\text{fus}}$$

$$-(340 \text{ mL} \cdot 1 \text{ g/mL})(4.18)(0 - 20.5) = (m_{\text{ice}})(333 \text{ J/g})$$

$$\frac{28424 \text{ J}}{333 \text{ J/g}} = m_{\text{ice}}$$

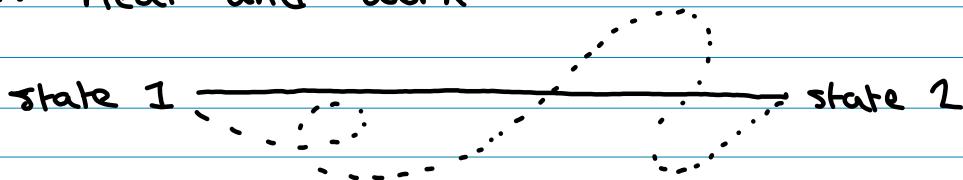
$$\boxed{m_{\text{ice}} = 85.4 \text{ g}}$$

*Note: if the ice started at -5°C , and we wanted everything to end up at 5°C :

$$-q_{\text{cola}} = q_{\text{ice}(-5 \rightarrow 0)} + q_{\text{ice(fus)}} + q_{\text{water}(0 \rightarrow 5)}$$

Different type of energy functions

- State functions
 - quantities describe present state of system
 - Does not depend on the systems past or future
 - Pathway independent (doesn't matter how system arrived in that state)
 - ex: Internal energy and enthalpy (NOT change)
- Path functions
 - Quantities that depend on pathway taken to change between 2 states
 - ex: heat and work

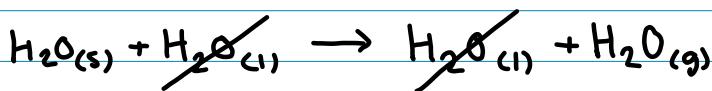
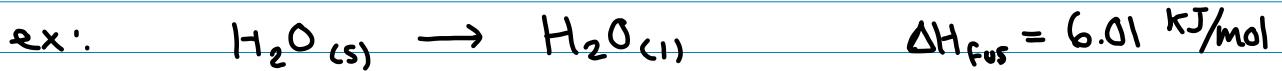


Determine Enthalpy of Reaction (ΔH_{rxn})

→ Hess's Law

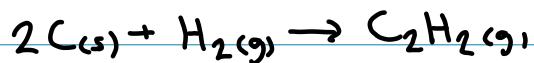
∴ enthalpy is a state fn, the change in enthalpy from initial to final state is pathway independent

Hess's Law = if a rxn is carried out in a series of steps, ΔH for the overall rxn will equal the sum of the ΔH for the individual steps.



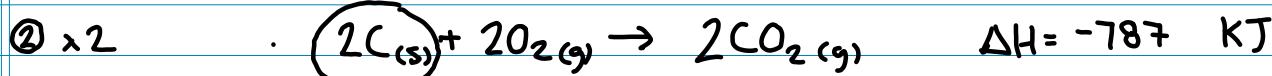
ex: Hess's Law

Calculate ΔH for the reaction:



Given.

- | | | |
|---|--|--------------------------------|
| ① | $2C_2H_2(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(l)$ | $\Delta H = -2599 \text{ KJ}$ |
| ② | $C(s) + O_2(g) \rightarrow CO_2(g)$ | $\Delta H = -393.5 \text{ KJ}$ |
| ③ | $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ | $\Delta H = -571.6 \text{ KJ}$ |



Determine the Enthalpy of Reaction (ΔH_{rxn})

→ Standard Enthalpies of formation

- Standard state = pure form of a substance at 1 atm and 25°C (298 K)
 - Metals are solid state: $M(s)$ (except $Hg(l)$)
 - Diatomic element: $I_2(s)$, $H_2(g)$, $N_2(g)$, $Br_2(l)$, $O_2(g)$, $Cl_2(g)$, $F_2(g)$
 - ↓ ice
 - ↓ beer
 - Compound:
 - Gas, $P = 1 \text{ atm}$
 - Sol'n, $c = 1 \text{ M}$
 - Pure substance, most pure/stable form
 - Element:
 - Form at which it exists at 1 atm and 25°C
 - If an element exists in more than one form under standard conditions, the most stable form of the element is used for the formation reaction
 - (ex: $C(\text{graphite})$ more stable than $C(\text{diamond})$)

Standard Enthalpy change (ΔH°) =

- enthalpy change when all reactants and products are in their standard states
 - degree symbol = carried out under standard conditions

Enthalpy of formation (heat of formation) (ΔH_f):

- enthalpy change associated with the formation of a compound from its constituent elements

Standard Enthalpy of Formation (ΔH_f°):

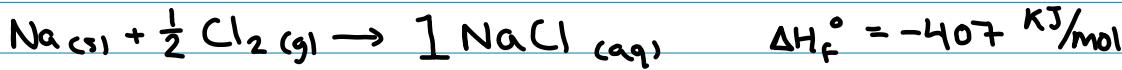
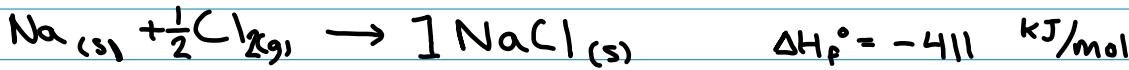
- change in enthalpy for the reaction that forms one mol of the compound from its elements with all substances in their standard states.

* Standard enthalpy formation for an element is zero.

ex. $C_{(\text{graphite})} : \Delta H_f^\circ = 0$, $C_{(\text{diamond})} : \Delta H_f^\circ = 3 \text{ kJ/mol}$ (b/c not standard)

ex: Write equations corresponding to the standard enthalpy of formation of $\text{NaCl}_{(s)}$ and $\text{NaCl}_{(\text{aq})}$

* Want 1 mol so balance accordingly



ex: Find $\text{NaCl}_{(s)} \rightarrow \text{NaCl}_{(\text{aq})}$



$$\Delta H_f^\circ = +411 \text{ kJ/mol}$$

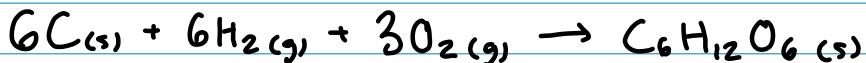


$$\Delta H_f^\circ = -407 \text{ kJ/mol}$$

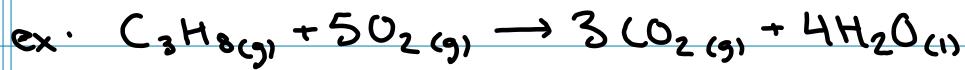


$$\Delta H_f^\circ = 4 \text{ kJ/mol}$$

ex: What does this mean: $\Delta H_f^\circ \text{ C}_6\text{H}_{12}\text{O}_6_{(s)} = -1275 \text{ kJ/mol}$



Using ΔH_f° to calculate ΔH_{rxn}°

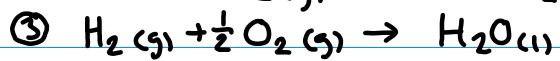
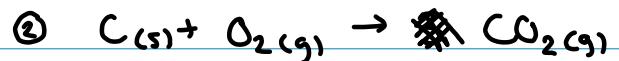


$$\Delta H_f^\circ C_3H_8(g) = -103.85 \text{ kJ/mol}$$

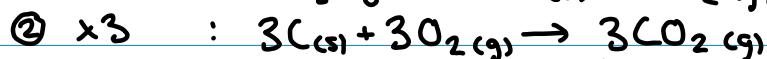
$$\Delta H_f^\circ O_2(g) = 0$$

$$\Delta H_f^\circ CO_2(g) = -393.5 \text{ kJ/mol}$$

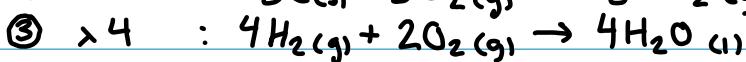
$$\Delta H_f^\circ H_2O(l) = -285.8 \text{ kJ/mol}$$



$$\Delta H^\circ = 103.85 \text{ kJ/mol}$$



$$\Delta H^\circ = -393.5 \text{ kJ/mol} \times 3 \text{ mol}$$



$$\Delta H^\circ = -285.8 \text{ kJ/mol} \times 4 \text{ mol}$$



$$\Delta H_{rxn}^\circ = -2220 \text{ kJ}$$

or: sum of ΔH_f° of products (what we form)

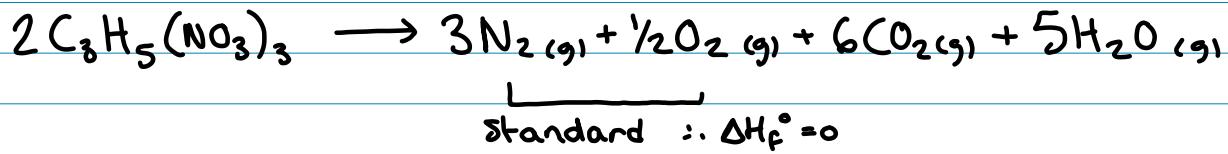
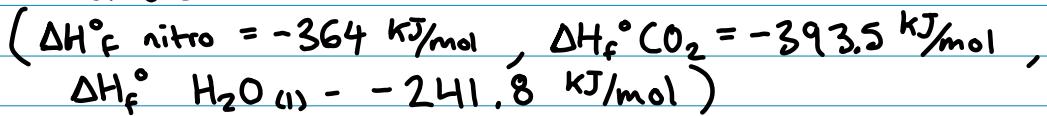
minus (-) sum of ΔH_f° of reactants (what we break)

$$\boxed{\Delta H_{rxn}^\circ = \sum n_p \Delta H_f^\circ (\text{products}) - \sum n_r \Delta H_f^\circ (\text{reactants})}$$

n_p, n_r = moles (based on coefficient)

$$\begin{aligned} \text{ex: } \Delta H_{rxn}^\circ &= [(3 \text{ mol } CO_2 \times -393 \text{ kJ/mol}) + (4 \text{ mol } H_2O \times -285.8 \text{ kJ/mol})] \\ &\quad - [(1 \text{ mol } C_3H_8 \times -103.85 \text{ kJ/mol})] \\ &= -2220 \text{ kJ} \end{aligned}$$

Ex. Calculate ΔH_{rxn}° when 10 g nitroglycerin is detonated:



$$\begin{aligned}\Delta H_{rxn}^\circ &= [(6 \text{ mol CO}_2 \times -393.5 \text{ kJ/mol}) + (5 \text{ mol H}_2\text{O} \times -241.8 \text{ kJ/mol})] \\ &\quad - [(2 \text{ mol } \xrightarrow{\Delta} \text{ -364 kJ/mol})] \\ &= \boxed{-2842 \text{ kJ}}\end{aligned}$$

$$10.0 \text{ g} \cdot \frac{\text{mol nitro}}{227.09 \text{ g}} \cdot \frac{-2842 \text{ kJ}}{2 \text{ mol nitro}} = \boxed{-62.57 \text{ kJ for 10.0 g}}$$

Determine the Enthalpy of Reaction (ΔH_{rxn})

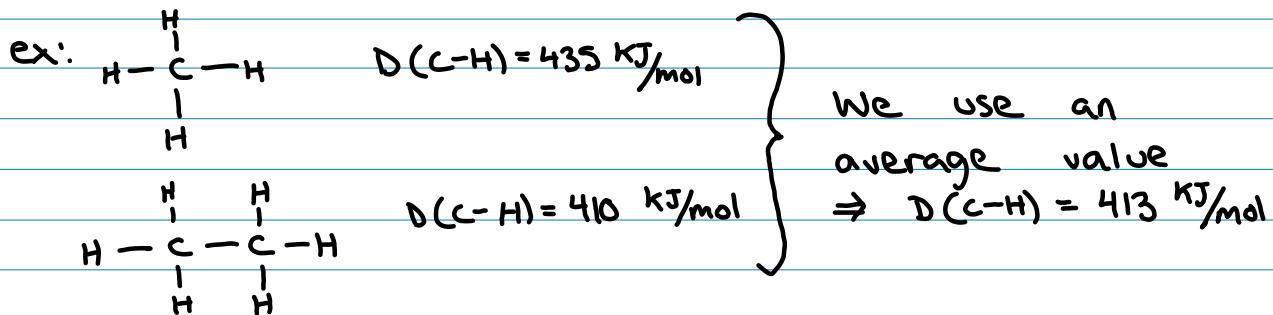
→ Bond Energies

Chemical reactions involve

- Breaking bonds in reactants (absorb + endo)
- Making bonds for products (release - exo)

- Bond Energy (D) = energy required to break one mol of a bond of a substance (always +)

We say that we "estimate" ΔH_{rxn} when we use bond energies b/c the values given to us are averages.



Bond energy is a measure of the ~~xxxxx~~ strength
→ Stronger the bond, the more energy to break it.
Bond length is the distance that separates 2 nuclei of bonded atoms
→ Bigger the bond length, the weaker the bond.

Bond	C-C	C=C	C≡C
Order	1	2	3
Average bond length (pm)	154	134	120
Average bond energy (kJ/mol)	347	614	839

require more energy to break

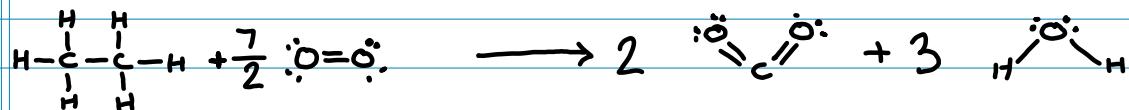
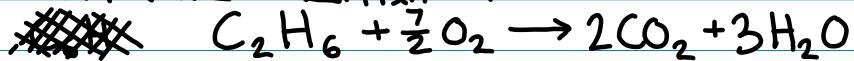
$$\Delta H_{rxn} = \sum n \times D(\text{bonds broken}) - \sum n \times D(\text{bonds formed})$$

Reactant Products

D : bond energy
 n : mol of bonds

- ⊕ \sum of all bonds broken in reactants
 (demands energy)
- ⊖ \sum of all bonds formed in products
 (releases energy)

ex: estimate ΔH_{rxn} for:



Broken

$$6 \text{ mol } C-H \times 413 \frac{\text{kJ}}{\text{mol}} = 2478$$

$$1 \text{ mol } C-C \times 348 \frac{\text{kJ}}{\text{mol}} = 348$$

$$\frac{7}{2} \text{ mol } O=O \times 495 \frac{\text{kJ}}{\text{mol}} = 1732.5$$

Formed

$$2 \times 2 \text{ mol } C=O \times 799 \frac{\text{kJ}}{\text{mol}} = 3196$$



$$3 \times 2 \text{ mol } H-O \times 463 \frac{\text{kJ}}{\text{mol}} = 2778$$

$$\Delta H_{rxn} = 4558.5 \text{ kJ} - 5974 \text{ kJ}$$

$$= \boxed{-1415.5 \text{ kJ}}$$