ENTHALPY CHANGE

CHAPTER 4

ENTHALPY

Please write

- **Is the <u>total</u> energy of a system.**

$$H = E_k + E_p$$

  - E_k= Kinetic energy.
    - Vibrational
    - Rotational
    - Translational

E due to motion

  - E_P= Potential energy
    - Attractive force b/w nucleons & electrons
    - E stored by the bonds between atoms & molecules.

- **∆H is the change in <u>total</u> energy of the system during a rxn or phase change.**
- **Most of the E exchanged is in the form of heat!**
- **Therefore we use the change in heat as a indicator of the change in enthalpy expressed per mol!**

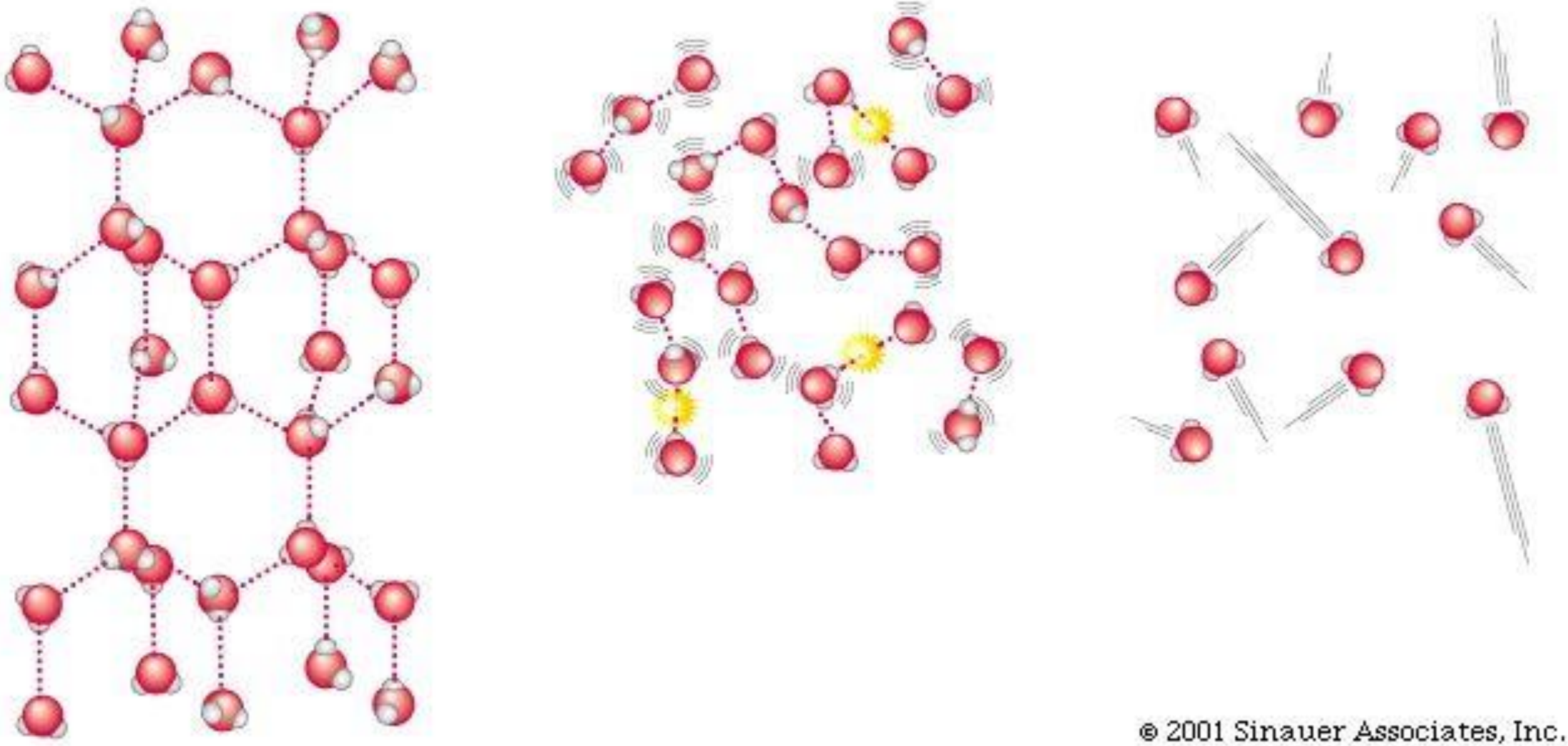
$$\frac{Q}{mol} = \Delta H$$

at constant T & P

(*a*) **Solid water (ice)**

(*b*) **Liquid water**

(*c*) **Gaseous water (steam)**



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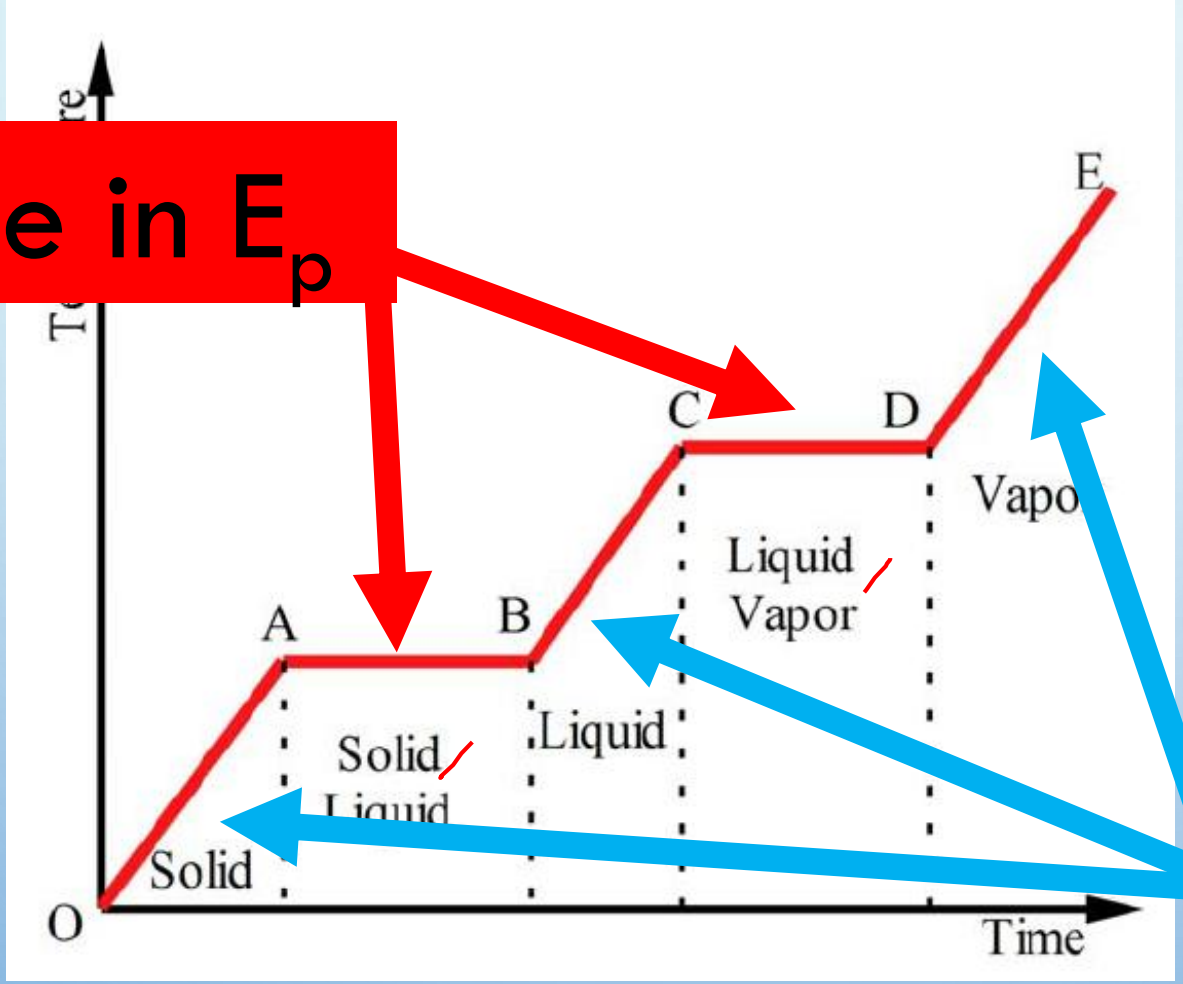
ΔH – PHASE CHANGES

Paste into notes and fill!

Change in E_p

Energy breaks intermolecular bonds



Energy increases the speed of molecules

Change in E_k

Please write

HOW TO CALCULATE ΔH MELTING ICE → VAPOUR

$Q_{ice} = mc\Delta T$ (c=2.05 J/g°C)

+

At the **melting point** $\Delta H = 6.01 kJ/mol$ until all the ice is melted!

+

$Q_{water} = mc\Delta T$ (c=4.19 J/g°C)

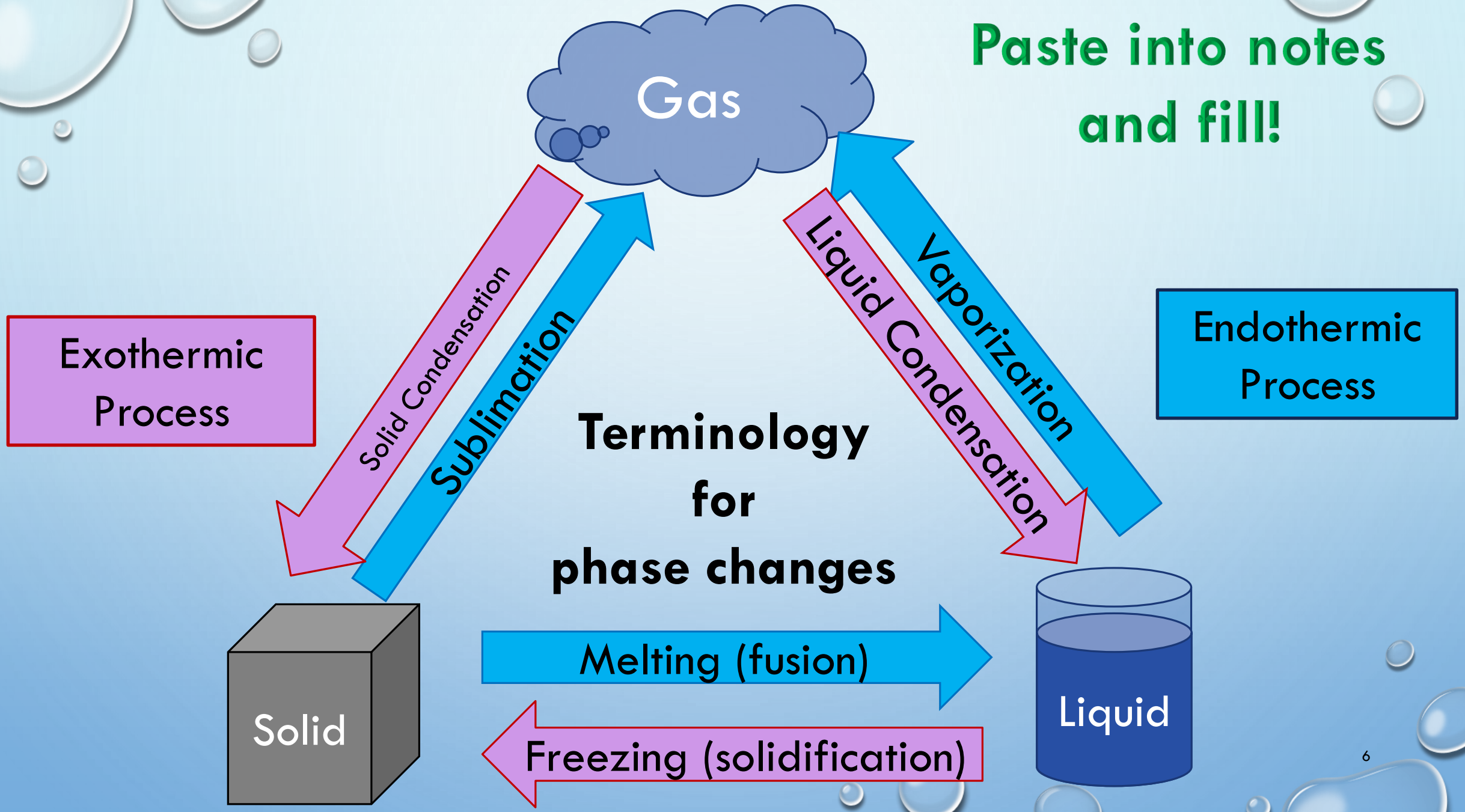
+

At the **boiling point** $\Delta H = 40.66\ kJ/mol$ until all the water is vaporised!

+

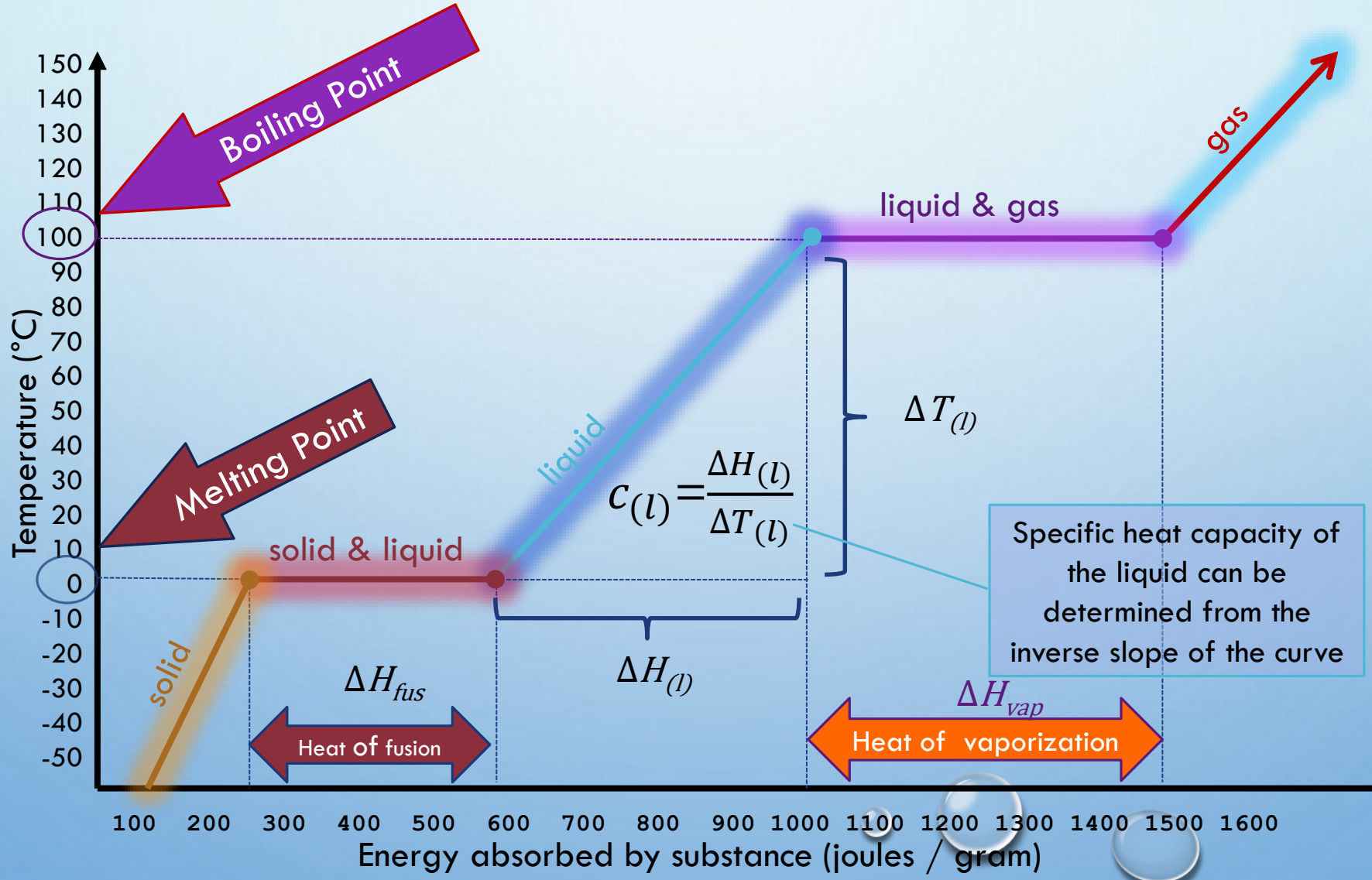
$Q_{vapour} = mc\Delta T$ (c=1.41 J/g°C)

Paste into notes and fill!



observe

HEAT CURVE OF A PURE SUBSTANCE



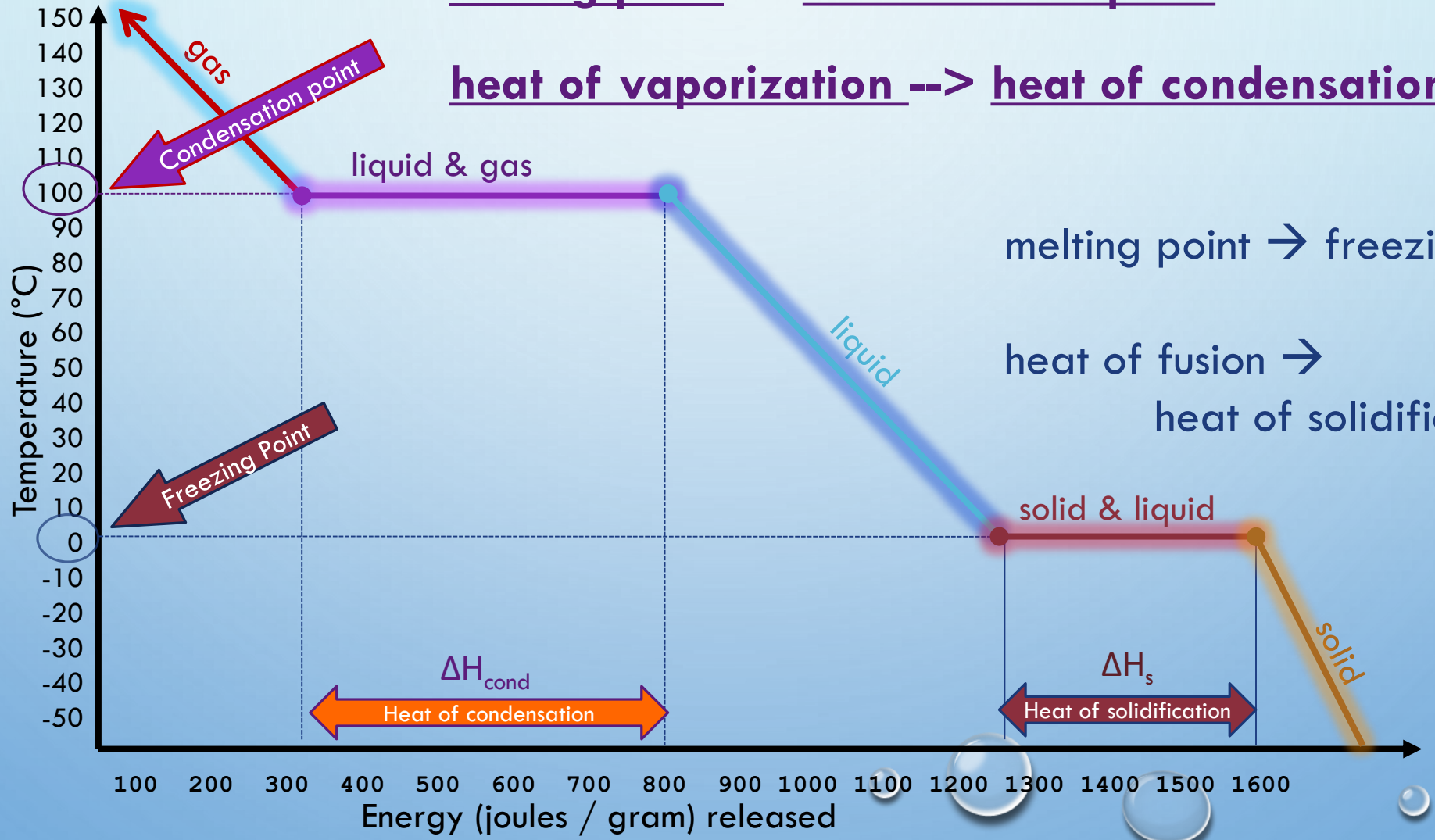
REVERSING A HEAT CURVE

observe

If instead we cool a hot gaseous substance….

boiling point → condensation point.

heat of vaporization --> heat of condensation.



melting point → freezing point.

heat of fusion →
heat of solidification.

IMPORTANT PTS FROM A HEAT CURVE:

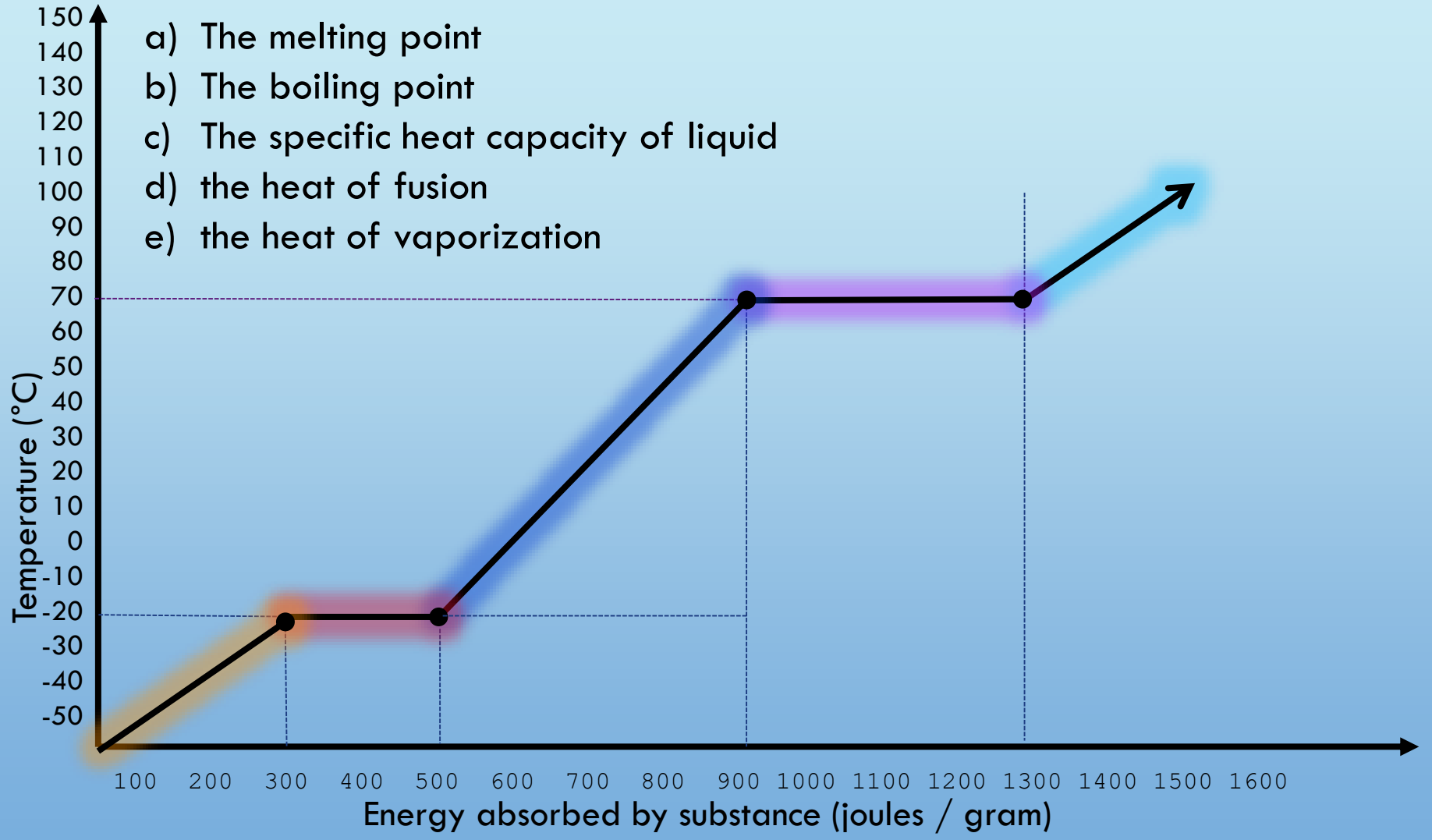
Please write

- The melting/freezing point temperature (1st plateau)
- The boiling point temperature/vaporization/condensation/ (2nd plateau)
- The heat of fusion (ΔH_{fus}) or solidification (ΔH_s) (change in x-axis)
- The heat of vaporization (ΔH_{vap}) or condensation (ΔH_{cond}) (x-axis)
- The specific heat capacity (c) of the solid or liquid substance.
  - Calculated from the $\Delta H/g$ and ΔT from the inverse slope
  - Since $Q=mc\Delta T$ & $Q/m = \Delta H(J/g)$ from the graph so
  - $c = \frac{\Delta H}{\Delta T}$

SAMPLE PROBLEM IMAGINARY HEAT CURVE

Use the heat curve to determine:

a) The melting point
b) The boiling point
c) The specific heat capacity of liquid
d) the heat of fusion
e) the heat of vaporization



SAMPLE PROBLEM IMAGINARY HEAT CURVE

Please glue into notes and solve

Use the heat curve to determine:

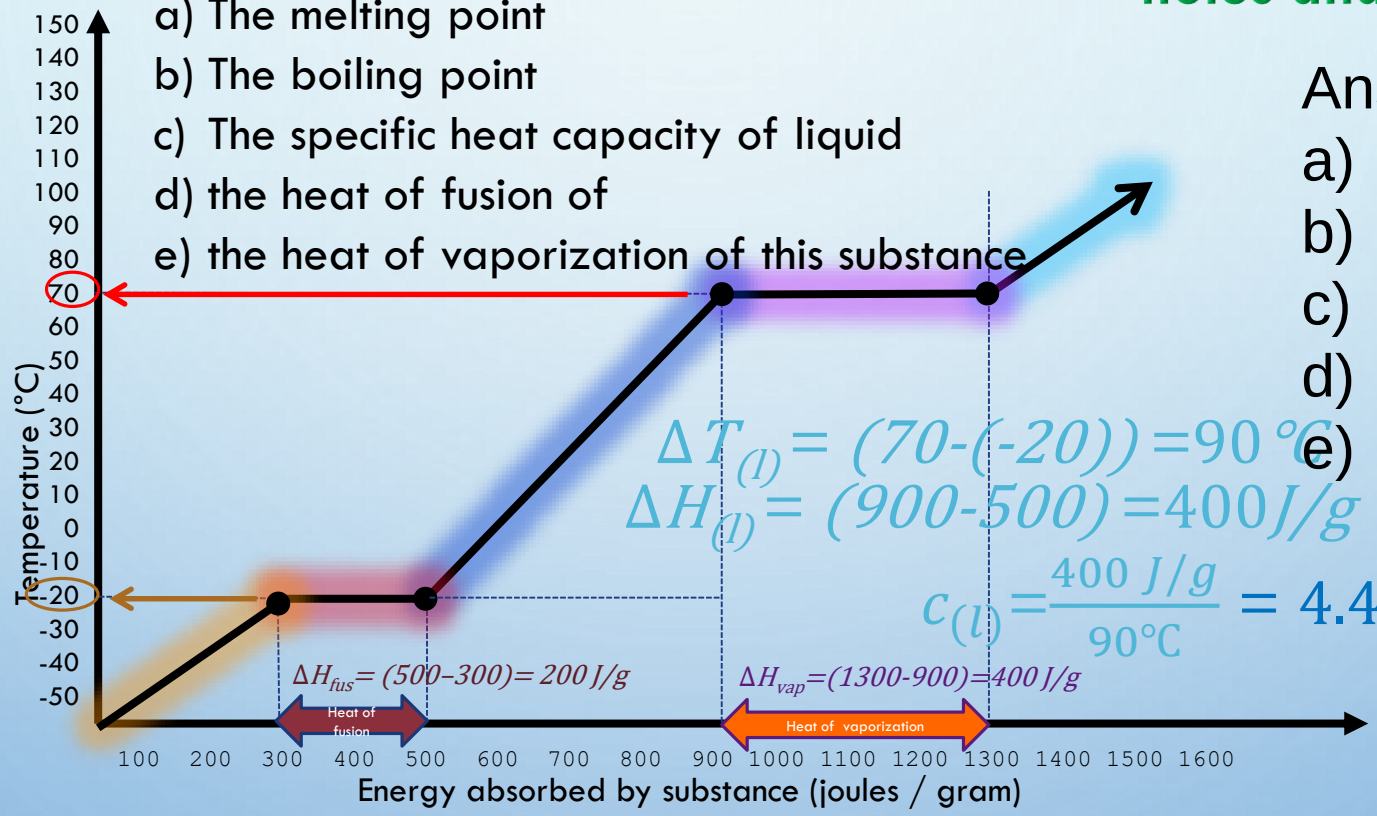
a) The melting point

b) The boiling point

c) The specific heat capacity of liquid

d) the heat of fusion of

e) the heat of vaporization of this substance



$\Delta T_{(l)} = (70\text{-}(\text{-}20)) = 90\,°C$

$\Delta H_{(l)} = (900\text{-}500) = 400\,J/g$

$c_{(l)} = \frac{400\ J/g}{90°C} = 4.44\ J/g°C$

Answers:

a) –20°C

b) +70°C

c) 4.44 J/g°C

d) 200 J/g*

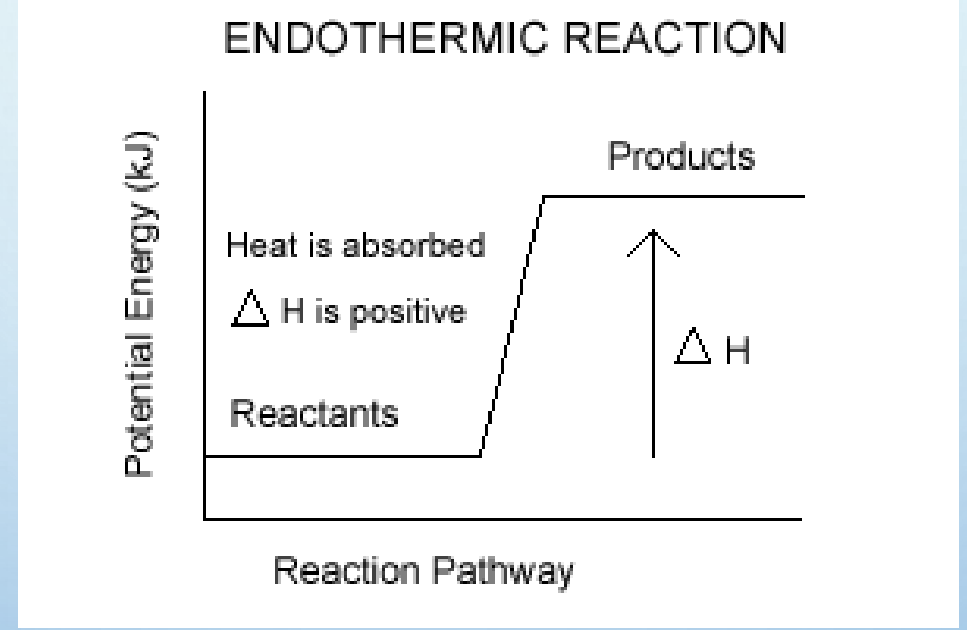
e) 400 J/g*

*Heat of fusion and vaporization are given in J/g.

To convert to the more standard form (J/mol) we could multiply this answer by the molar mass.

Today:

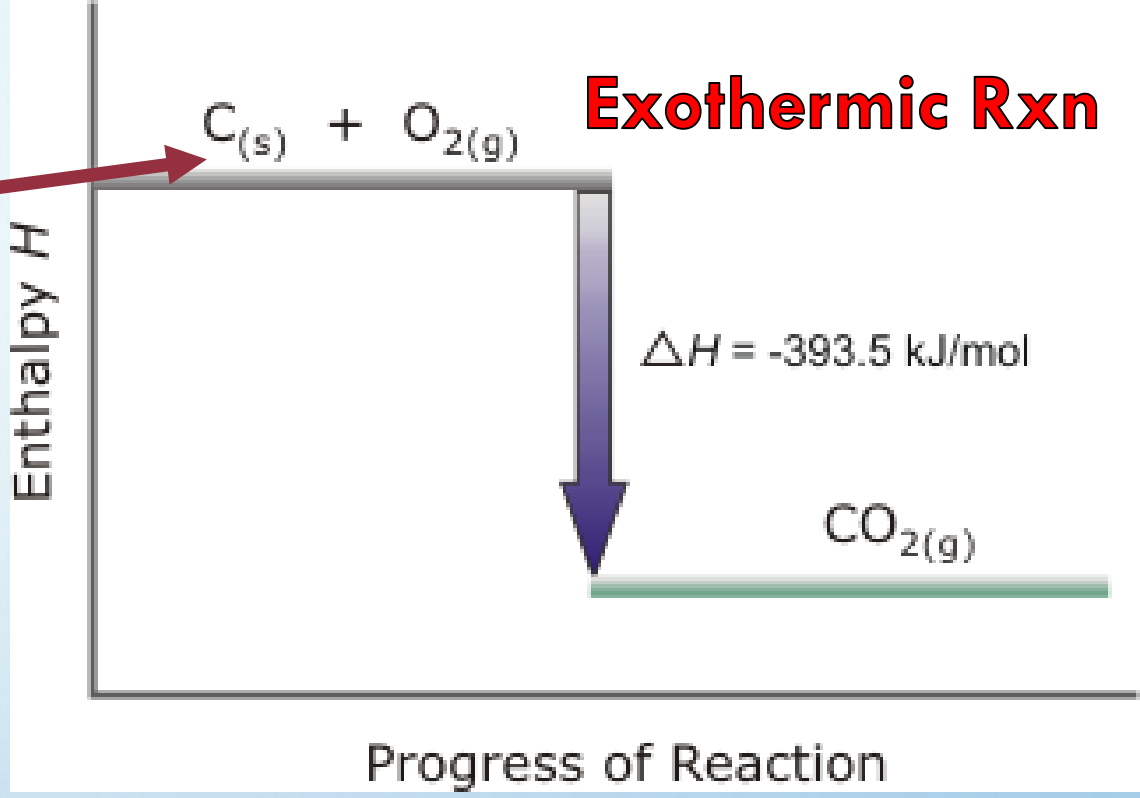
1. Expressing ΔH as a simplified graph



2. Expressing ΔH within a rxn

Please write/sketch

- **The bonds in C + O_2 contain more energy than the bonds in CO_2.**
- **Energy is released (exothermic)(ΔH is neg)**



- **Written as:**

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} + 393.5$ kJ/mol

or

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -393.5$ kJ/mol

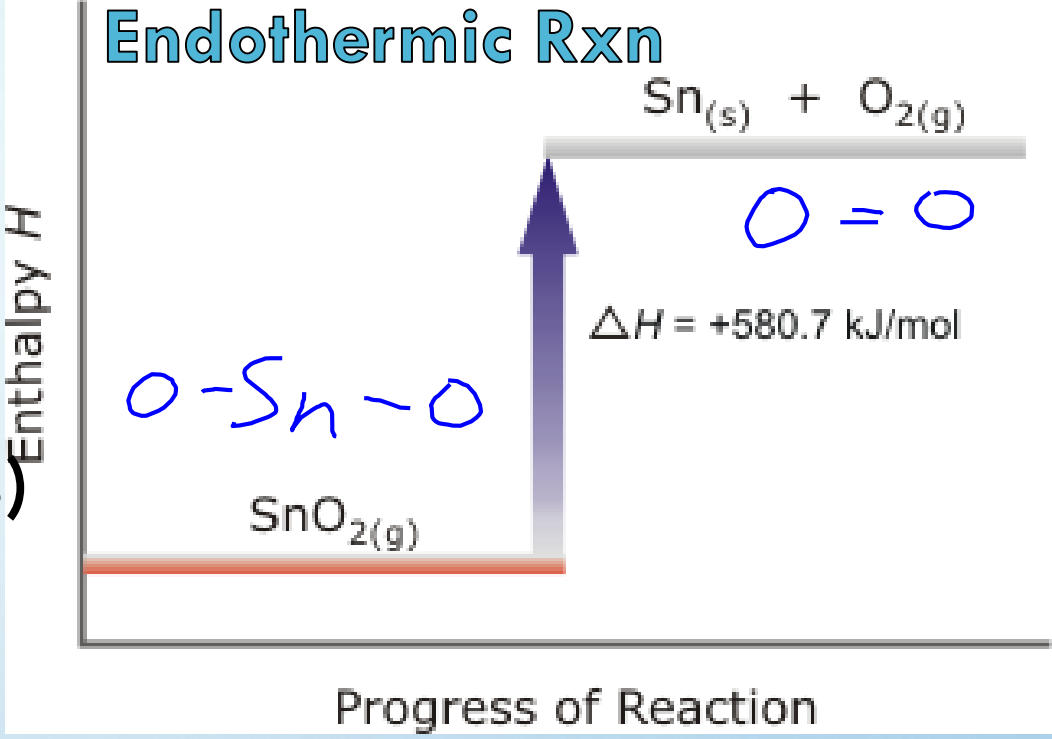
Please write/sketch

- **The bonds in SnO_2 contain <u>less</u> energy than the bonds in Sn + O_2.**
- **Energy is absorbed (endothermic)(ΔH is pos)**
  - **Written as:**

$SnO_{2\,(g)}$ + 580.7 kJ/mol →$Sn_{(s)}$ + $O_{2\,(g)}$

or

$SnO_{2\,(g)}$ →$Sn_{(s)}$ + $O_{2\,(g)}$ ΔH= +580.7 kJ/mol



EXAMPLES

Please write & do this exercise

Determine the sign of ΔH; state "exothermic" or "endothermic" & draw energy diagram for each of the following:

1. $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(g)} + 285.8kJ/mol$
2. $40.7kJ/mol + H_2O_{(l)} \rightarrow H_2O_{(g)}$
3. When nitroglycerine decomposes, it causes a violent explosion, releasing $5.72 \times 10^3 kJ$ of heat for each mole.

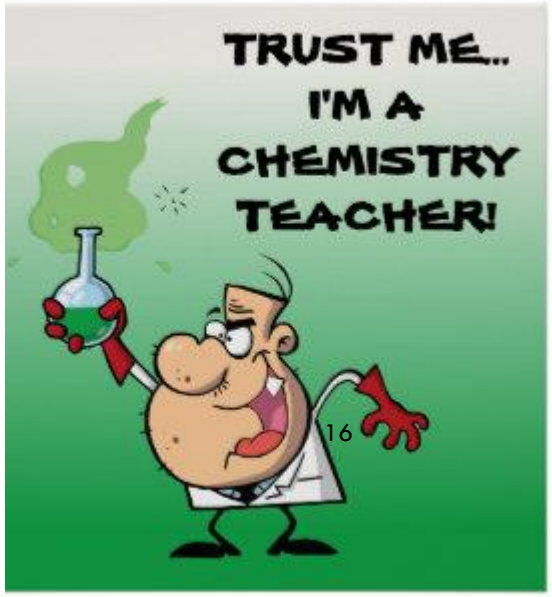
$$C_3H_5(NO_3)_3 \rightarrow 3CO_2 + 5/2\ H_2O + \frac{1}{4}O_2 + 3/2N_2$$

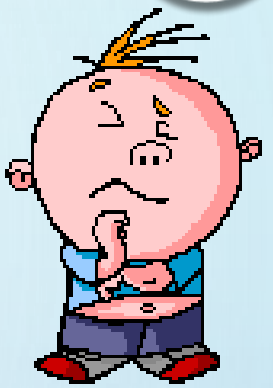
1. $H_2(g) + ½\ O_2(g) \rightarrow H_20(g) + 285.8kJ$

$\Delta H = -285.8$ KJ → IS NEGATIVE

REACTION IS EXOTHERMIC

Graph





2. $40.7kJ + H_2O(l) \rightarrow H_2O(g)$

ΔH IS POSITIVE

REACTION IS ENDOTHERMIC

Graph

3. $C_3H_5(NO_3)_3 \rightarrow 3CO_2 + 2.5\ H_2O + \frac{1}{4}O_2 + 1.5N_2$

ΔH IS NEGATIVE

REACTION IS EXOTHERMIC

We will be studying…..

Expressing ΔH as a graph & calculating in 4 different ways

1. **Q = mcΔT & $\Delta H = \frac{Q}{n}$ Q = energy expressed in Joules.** ☑

   ΔH = energy expressed in Joules/mol.

2. **Graphs**

3. **Using table with ΔH_f** $\Delta H_{rxn} = \Delta H_f(products) - \Delta H_f(reactants)$

4. **Using bond energies** $\Delta H_{rxn} = (\sum E\ of\ broken\ bonds) - (\sum E\ of\ bonds\ formed)$

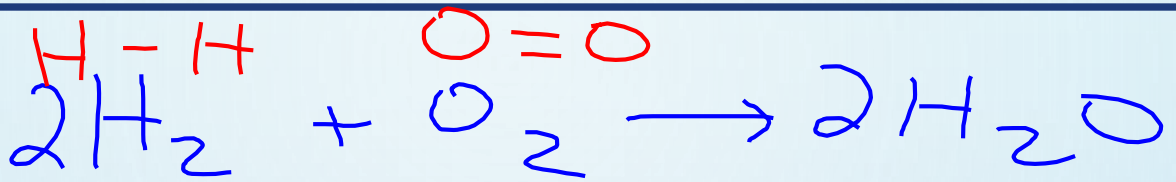
5. Hess's Law (adding known equations)

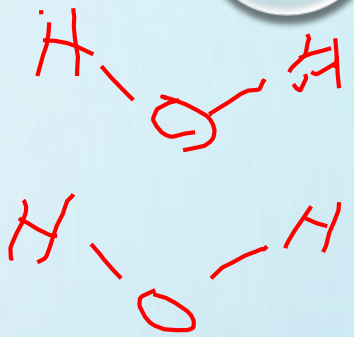
Please write

- **Using a calorimeter chemists have formed appendices @SATP for:**
  - **Heat of formation (ΔH_f) = energy stored in a substance during its formation from elements**
  - **Heat of fusion (ΔH_{fus})** melting
  - **Heat of vaporisation (ΔH_{vap})** boiling
  - **Heat of dissolution (ΔH_d)**
  - **Heat of combustion (ΔH_{comb})**
  - **Heat of a certain reaction (ΔH_{rxn})**
  - **etc**

Textbook appendix 8

HAND-OUT BLUE TABLE!





- Please note!
- The **heat of formation (ΔH_f) is the energy stored in a substance during its formation from elements.**
- **So substances in their elemental form have a $\Delta H_f = 0$.**
  - **ΔH_f of $O_2 = 0$.**
  - **ΔH_f of Ag = 0. The solid silver metal not the ion!**
  - **ΔH_f of CO= -110.5 kJ/mol because it is made from C + O_2**

How do you calculate ΔH_{rxn} from ΔH_f?

Please write

$$\Delta H_{rxn} = \Delta H_f(products) - \Delta H_f(reactants)$$

Look these up on the blue table!

- Ex 1. $CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow CO_{2\,(g)} + 2H_2O_{\,(l)}$ + **890.3 kJ/mol**

$$\Delta H_{rxn} = \Delta H_f(products) - \Delta H_f(reactants)$$

$$= (-393.5 + 2(-285.8)) - ((-74.8) + 2(0))$$

$$= (-965.1) - (-74.8)$$

$$= -890.3 \text{ kJ/mol of methane}$$

The values must be multiplies by the coefficients!

Exothermic!

- $\Delta H = \frac{Q}{n}$ ☑
- Graph ☑
- ΔH_f ☑
- Bond energies
- Hess's Law

Please write

- Ex 2. $H_{2\,(g)} + Cl_{2\,(g)} \rightarrow 2HCl_{\,(g)}$ ΔH_{rxn} **= - 184.6 kJ/mol**

$$\Delta H_{rxn} = \Delta H_f(products) - \Delta H_f(reactants)$$

$$= (2(-92.3))-(0 + 0)$$

$$= (-184.6) - (0)$$

$$= -184.6\ kJ/mol\ of\ hydrogen$$

Exothermic!

Please write

- Graph ☑
- ΔH_f ☑
- Bond energies ☑
- Hess's Law

How do you calculate ΔH_{rxn} from bond energies?

- Find the energy difference in making and breaking bonds.
- Based on average bond enthalpies.
- Provides a rough estimate!

$$\Delta H_{rxn} = (\sum E\ of bonds\ broken\ ) - (\sum E\ of\ bonds\ formed)$$

Ex 3. $H_{2\,(g)} + Cl_{2\,(g)} \rightarrow 2HCl_{\,(g)}$

$\Delta H_{rxn} = (\sum E\ of bonds\ broken\ ) - (\sum E\ of\ bonds\ formed)$

$= (436 + 243)\text{-}(2(432))$

$= (679) - (864)$

$= -185\ kJ/mol\ of\ hydrogen$

2x

Bond	Energy
H-H	436 kJ/mol
H-O	460 kJ/mol
H-F	570 kJ/mol
H-Cl	432 kJ/mol
C-H	413 kJ/mol
C-C	347 kJ/mol
C=C	607 kJ/mol
C-O	358 kJ/mol
O=O	498 kJ/mol
C=O	745 kJ/mol
Cl-Cl	243 kJ/mol
N=N	418 kJ/mol
N=O	631 kJ/mol

P 419 →

Use bond energies to determine the enthalpy of the following rxns.

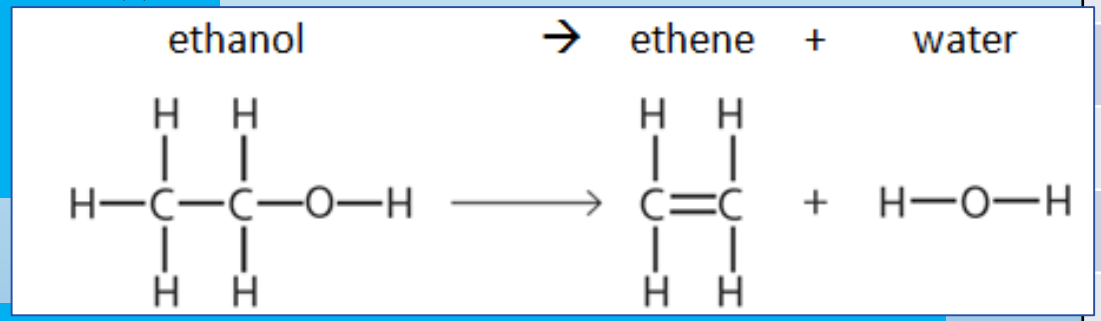
$2H_2 + O_2 \rightarrow 2\ H_2O$

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

$= (2(436) + 498) - (4(460))$

$= (1370) - (1840)$

$= -470\ kJ/mol$



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

$= (5(413)+347+358+460) - (4(413)+607+2(460))$

$= (3230) - (3179)$

$= 51\ kJ/mol$

Lewis dot diagrams help to determine what bonds are present.

Please write

Bond	Energy
H-H	436 kJ/mol
H-O	460 kJ/mol
H-F	570 kJ/mol
H-Cl	432 kJ/mol
C-H	413 kJ/mol
C-C	347 kJ/mol
C=C	607 kJ/mol
C-O	358 kJ/mol
O=O	498 kJ/mol
C=O	745 kJ/mol
Cl-Cl	243 kJ/mol
N=N	418 kJ/mol
N=O	631 kJ/mol

Please write

We have found four ways to calculate enthalpy, ΔH:

- **Q = mcΔT & $\Delta H = \frac{Q}{n}$ Q = energy expressed in Joules.**

  ΔH = energy expressed in Joules/mol.

- $\Delta H_{rxn} = \Delta H_f(products) - \Delta H_f(reactants)$
- $\Delta H_{rxn} = (\sum E\ of\ broken\ bonds) - (\sum E\ of\ bonds\ formed)$
  - Energy is needed to break bonds but is released when bonds are formed.
  - Therefore the equation is energy absorbed – energy released.
    - ΔH_{rxn} = positive # means more E is absorbed ∴ endothermic rxn
    - ΔH_{rxn} = negative # means more E is released ∴ exothermic rxn
- Hess's Law

To Make:

$$S_{(s)} + \frac{3}{2} O_{2(g)} \rightarrow SO_{3(g)} \qquad \Delta H = ?$$

- SOME REACTIONS OCCUR IN MULTIPLE STEPS.

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \qquad \Delta H = -296.8kJ$$

$$SO_{2(g)} + ½\ O_{2(g)} \rightarrow SO_{3(g)} \qquad \Delta H = -99.2kJ$$

- EACH STEP HAS AN ENTHALPY VALUE.

Please write

Hess' Law of Constant Heat Summation:

- **The enthalpy of a rxn is the same whether it happens in one step or in many.**
- **Therefore enthalpy values of known rxns can be added to give the enthalpy of a needed rxn.**

$$S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \qquad \Delta H = -296.8\text{kJ}$$

$$+ \quad SO_{2(g)} + \tfrac{1}{2} O_{2(g)} \rightarrow SO_{3(g)} \qquad \Delta H = -99.2\text{kJ}$$

$$S_{(s)} + \frac{3}{2} O_{2(g)} \rightarrow SO_{3(g)} \qquad \mathbf{\Delta H = -396kJ}$$

You are given....

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -393.5$ kJ/mol

$CO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -283.0$ kJ/mol

$C_{(s)} + \frac{1}{2}O_2 \rightarrow CO_{2(g)}$ $\Delta H = -393.5$ kJ/mol

flip

$+ CO_{2(g)} \rightarrow CO_{(g)} + \frac{1}{2} O_{2(g)}$ $\Delta H = +283$ kJ/mol

We want → **$C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)}$** **$\Delta H = -110.5$ kJ/mol**

Please write

- **Rules for rearranging equations:**
  - **Step 1: Rewrite so that the reactants & products are on the desired side. (Switch sign of ΔH when reversing an equation)**
  - **Step 2: Adjust for the # of moles by multiplying the entire equation. (You also multiply the ΔH value!)**
  - **Step 3: Cancel/reduce what appears on both sides.**
  - **Step 4: add up the ΔH values.**

- GIVEN: $2\ Al_{(s)} + 3/2\ O_{2(g)} \rightarrow Al_2O_{3(s)}$ $\Delta H = -1675$ kJ

$2\ Fe_{(s)} + 3/2\ O_{2(g)} \rightarrow Fe_2O_{3(s)}$ $\Delta H = -838$ kJ

Rewrite as is.

$2Al_{(s)} + 3/2O_{2(g)} \rightarrow Al_2O_{3(s)}$ $\Delta H = -1675$ kJ

Flip & reverse sign

$Fe_2O_{3(s)} \rightarrow 2\ Fe_{(s)} + 3/2\ O_{2(g)}$ $\Delta H = +838$ kJ

+

$Fe_2O_{3(s)} + 2\ Al_{(s)} \rightarrow Al_2O_{3(s)} + 2\ Fe_{(s)}$ $\Delta H = -837$ kJ

Ex. The formation of nitric acid is given by the following equation:

$$12NH_3 + 21O_2 \rightarrow 8HNO_3 + 4NO + 14H_2O$$

Given the equations below, calculate the ΔH for nitric acid.

$NH_3 + 5/4\ O_2 \rightarrow NO + 3/2H_2O$ ΔH = -293 kJ/mol

$NO + ½\ O_2 \rightarrow NO_2$ ΔH = -59 kJ/mol

$NO_2 + 1/3H_2O \rightarrow 2/3HNO_3 + 1/3NO$ ΔH = -45 kJ/mol

$12\ NH_3 + 15\ O_2 \rightarrow 12\ NO + 14\ H_2O$ $\Delta H = -3516$ kJ

$12\ NO_2 + 4\ H_2O \rightarrow 8\ HNO_3 + 4\ NO$ $\Delta H = -540$ kJ

$12\ NO + 6\ O_2 \rightarrow 12\ NO_2$ $\Delta H = -708$ kJ

+

$12NH_3 + 21O_2 \rightarrow 8HNO_3 + 4NO + 14H_2O$ $\Delta H = -4{,}764$ kJ