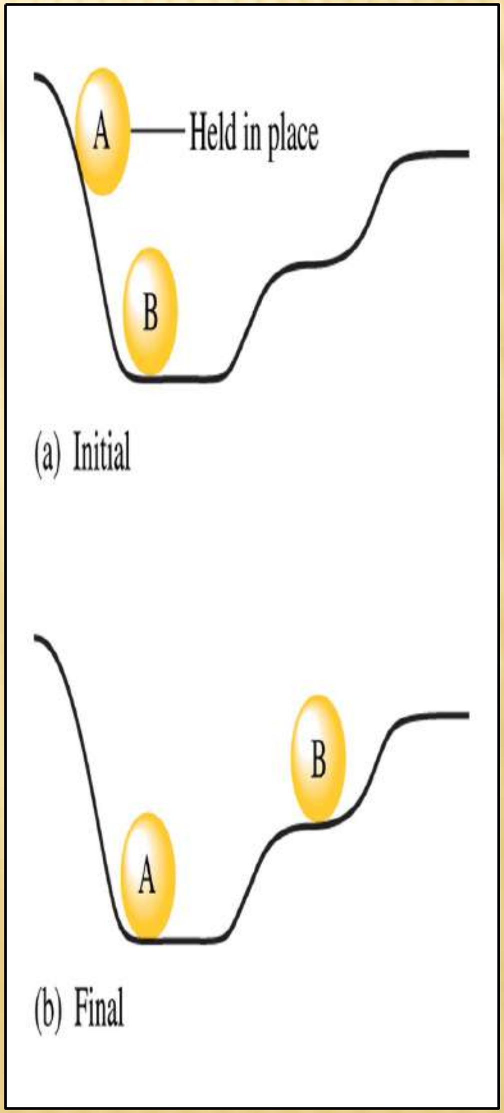
Chapter 6

THERMOCHEMISTRY

ENERGY DEFINITIONS

- Energy – capacity to do work or supply heat
- Law of Conservation of Energy – energy cannot be created nor destroyed but can be converted between forms.
- 1st Law of Thermodynamics – total energy of the universe is constant.
- Potential Energy – energy of position
- Kinetic Energy – energy of motion ($KE = \frac{1}{2} mv^2$)



ENERGY DEFINITIONS

- Heat – transfer of E due to temperature difference.
- Work – force acting over distance (more later)
- State function – depends only on present state
  - Energy is a state function (doesn't depend on *how*)
  - Work is not a state function (depends on *how*)

ENERGY OF THE UNIVERSE

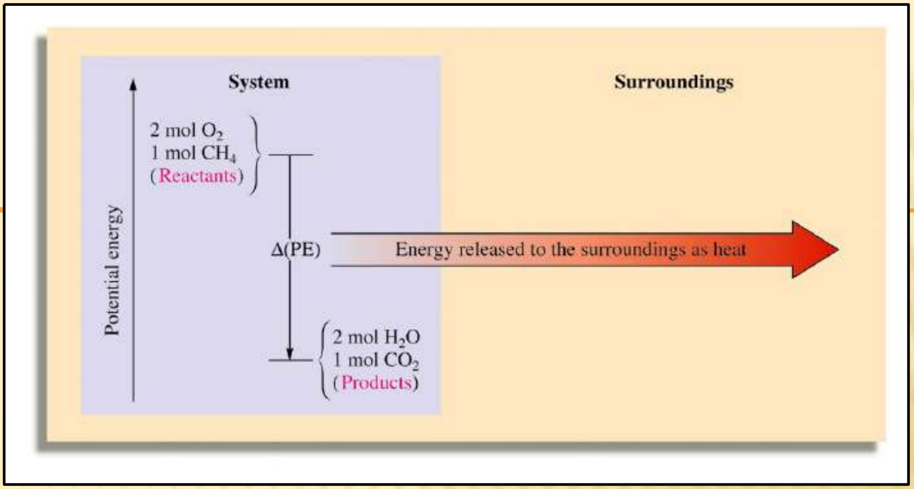
- The universe is made of 2 things

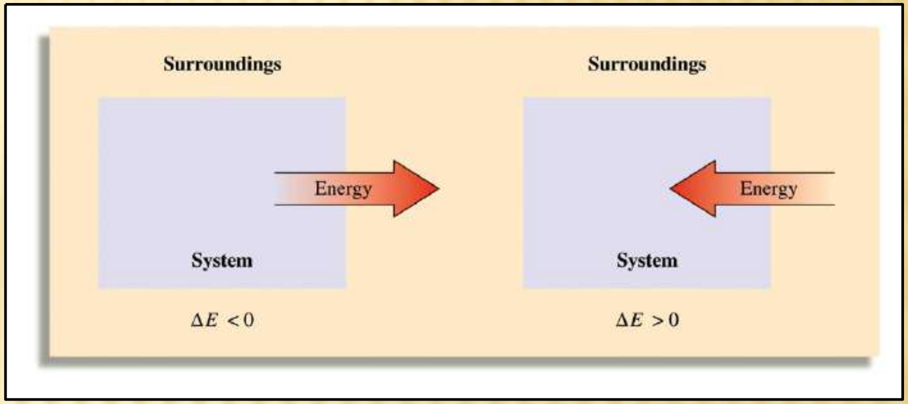
1. <u>System</u> – part of universe interested in
   - Usually the reactants and products

2. <u>Surroundings</u> – the rest of the universe
   - Everything else

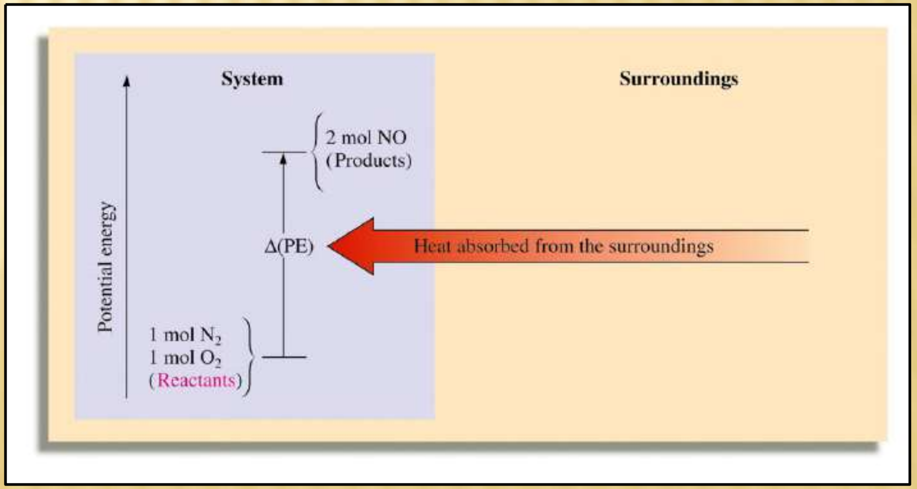
MOVEMENT OF HEAT

- Exothermic – energy flows out of the system into the surroundings
  - more E in reactants





- Endothermic – energy flows into the system from the surroundings
  - more E in products



INTERNAL ENERGY (E)

- The sum of the kinetic and potential energies
- Can be changed by heat, work, or both
- $\Delta E = q + w$
  - ΔE = Change of system's internal energy
  - q = heat
  - w = work
- Always seen from system's POV
- (-) negative sign means energy leaves system

HW: 21-24a

CALCULATING ΔE

- 1. Absorbs 15 kJ of heat while doing 30 kJ of work.
- 2. 45 kJ of work are done by surroundings while losing 45 kJ of heat.
- 3. An exothermic rxn evolving 10 J of heat while doing 10 J of work.
- 4. The surroundings do “X” joules of work while the system absorbs “Y” joules of heat.

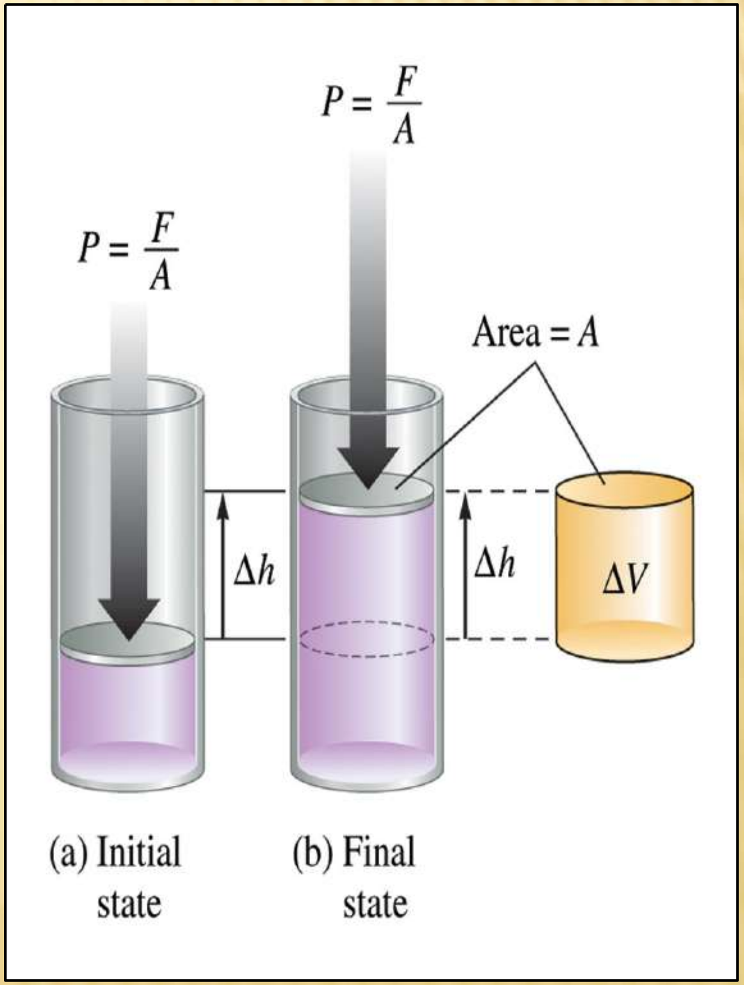
PV WORK EXPANSION/COMPRESSION OF GAS

- w = force x distance

  distance = Δh
- w = force x Δh

  P = F/A or F = P x A
  - w = P x A x Δh

  V = A x h ΔV = A x Δh
- w = PΔV (but what about sign)
- w = - PΔV



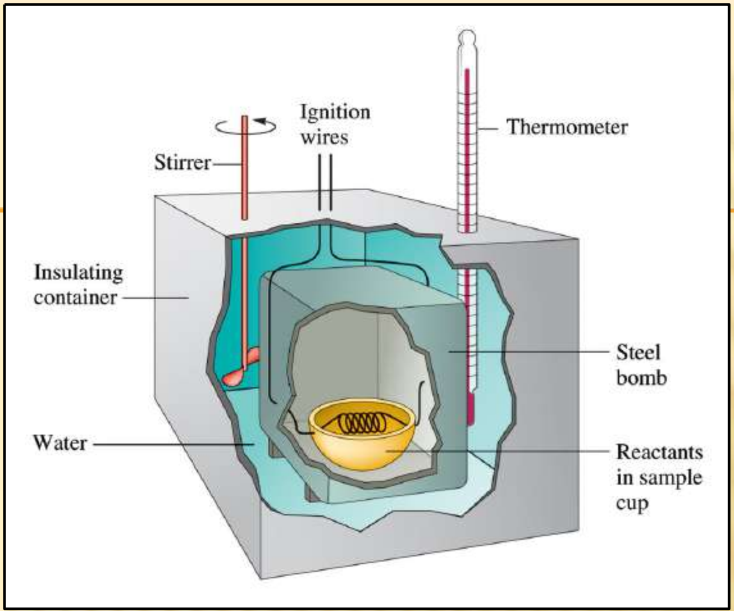
PV WORK, HEAT, AND INTERNAL ENERGY

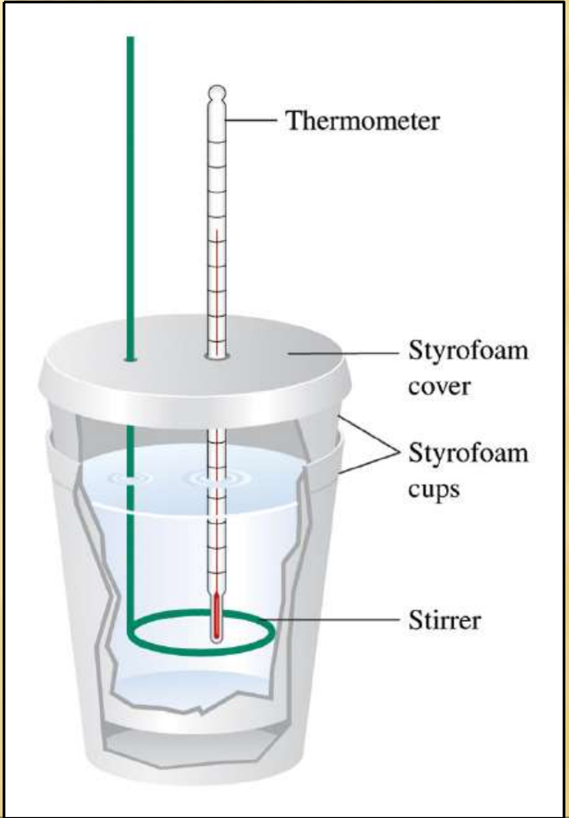
1. Calculate the work associated with a gas being compressed from 30.0 L to 22.4 L at a constant 2.50 atm.
2. Assume that a gas absorbs 4.00×10^6 J of heat while expanding from 45.0 L to 105 L at a constant 1.00 atm. Calculate the change in internal energy (ΔE) for the process. 1 L · atm = 101.3 J

HW: 24 - 28

CALORIMETRY

- The amount of heat absorbed or released during a physical or chemical change can be measured, usually by the change in temperature of a known quantity of water in a calorimeter.





$q = mc\Delta T$

CALORIMETRY

- Heat Capacity – heat absorbed/ temp increase

  $C = \Delta H/\Delta T$

- Specific Heat Capacity – heat capacity per gram

  $c = J/g\cdot {}^{o}C$ or $J/g\cdot K$

- Molar Heat Capacity – heat capacity per mole

  $c = J/mol\cdot {}^{o}C$ or $c = J/mol\cdot K$

- **$q = mc\Delta T$**

HW: 41-44

EXAMPLES

1. How much heat is needed to heat 25.0 g of H_2O from 40°C to 75°C? (c_{H2O} = 4.184 J/g°C)
2. What volume of water can be heated from 405K to 475K with 7.00kJ of heat. (1 mL = 1 g)
3. 45.0g of solid aluminum at 45°C releases 675J of heat. What will the final temperature of the aluminum be? (c_{Al} = 0.89 J/gK)
4. What is the specific heat capacity of a fictional substance if 48.0J are needed to raise the temperature of 5.00g by 25.0°C?
5. If the molar mass of the unknown substance in #4 is 46 g/mol, calculate the molar heat capacity

HW: 45, 49, 50, 51

REAL EXAMPLES

#46: Bio experiment requires a 37.0°C water bath. The temp of the cold tap water is 22.0°C, and the temp of the hot water tap is 55.0°C. If a student starts with 90.0g of cold water, what mass of hot water must be added to reach 37.0°C?

#52: 1.60g of NH_4NO_3 is mixed with 75.0g of water at an initial temp of 25.00°C. After dissolution the final temp of the calorimeter contents is 23.34°C. Assuming solution's heat capacity is same as water and no heat loss calculate the enthalpy change (heat) for the dissolution in units of kJ/mol.

ENTHALPY (H)

- H = E + PV(This is the definition)
- ΔH = ΔE + PΔV(at constant pressure)
- ΔE = q + wor ΔE = q – PΔV
- Therefore: q = ΔE + PΔV

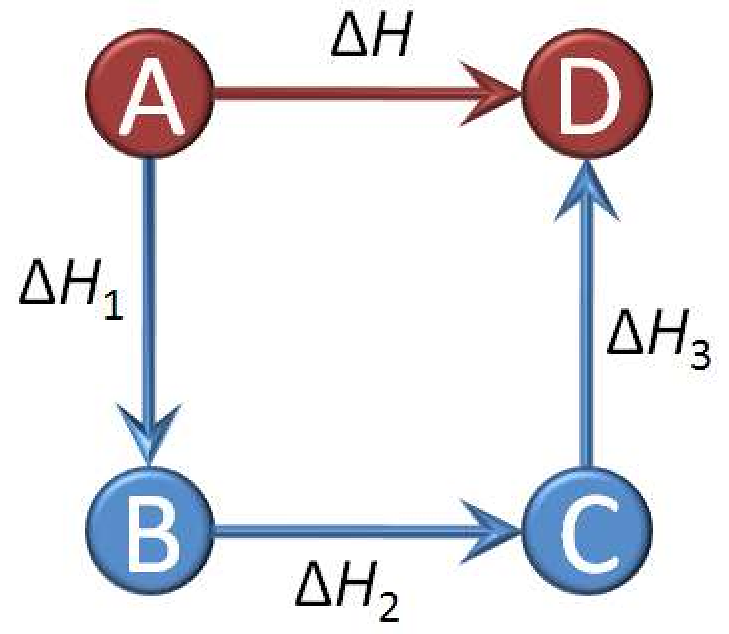
  ΔH = ΔE + PΔV
- So: enthalpy (H) is kindaish the same as heat
- H is often called the “heat of reaction”

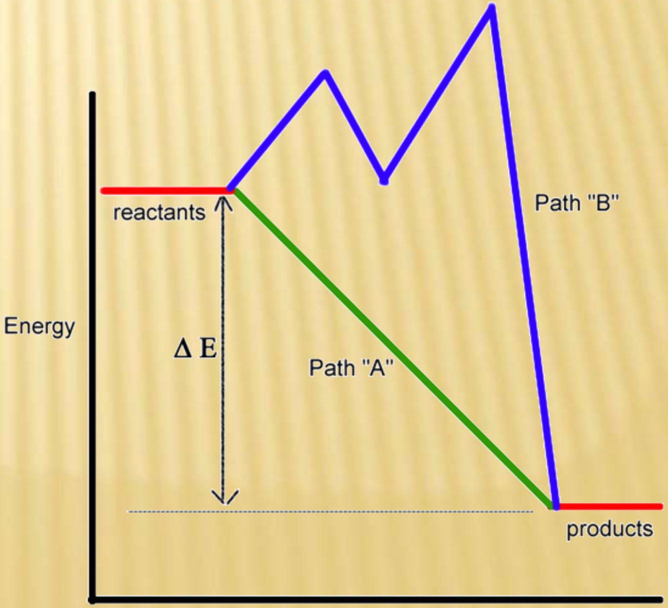
HESS'S LAW

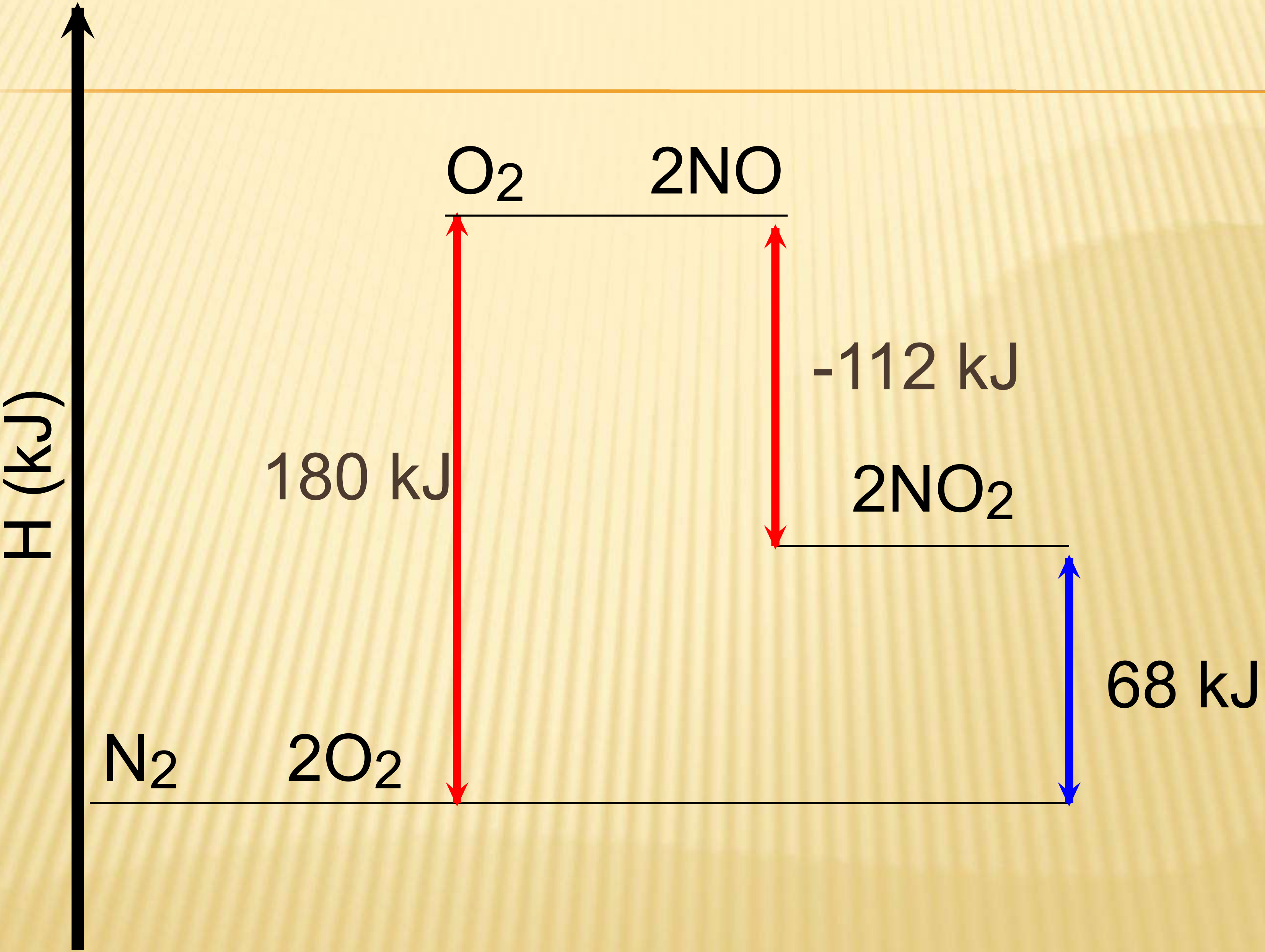
- Enthalpy is a state function.
- Therefore: ΔH is the same no matter the path taken.
- We can add equations to get the desired final product, and add the ΔH

<u>Two rules</u>

- If the reaction is reversed the sign of ΔH is changed
- If the reaction is multiplied, so is ΔH







H (kJ)

O_2 2NO

-112 kJ

180 kJ

$2NO_2$

68 kJ

N_2 $2O_2$

HESS'S LAW EXAMPLES

- Calculate ΔH for the combustion of methane:

$$CH_4 \quad + \quad 2\,O_2 \quad \rightarrow \quad CO_2 \quad + \quad 2\,H_2O$$

Reaction	ΔH^o
$C + 2H_2 \rightarrow CH_4$	-74.80 kJ
$C + O_2 \rightarrow CO_2$	-393.50 kJ
$H_2 + \frac{1}{2}\,O_2 \rightarrow H_2O$	-285.83 kJ

$\Delta H_{rxn} = -\,890.36$ kJ

MORE HESS

HW: 33,35,60,61,63,64

Calculate the ΔH:

$$N_2O_5 + H_2O \rightarrow 2\ HNO_3$$

Reaction	**ΔH°**
$H_2 + 1/2\ O_2 \rightarrow H_2O$	–285.8kJ
$½\ N_2 + 3/2\ O_2 + ½\ H_2 \rightarrow HNO_3$	–174.1 kJ
$2N_2 + 5\ O_2 \rightarrow 2\ N_2O_5$	+ 28.4kJ

STANDARD ENTHALPIES OF FORMATION

ΔH_f = change in enthalpy for the formation of 1 mole of a compound from its elements with all substances in their standard states.

Standard States

- **Compound:**
  - Gas is exactly 1 atmosphere of pressure
  - Pure liquid or solid
  - Substance in solution, concentration is 1 M
- **Element:**
  - The form the element is in at 1 atm and 25^{o}C

STANDARD ENTHALPIES OF FORMATION

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

- Shortcut for adding the reactions together
- Notes:
  - ΔH_f for an element is zero. WHY?
  - Need to multiply by ΔH by the # of moles needed

Calculation of Heat of Reaction

Calculate ΔH for the combustion of methane, CH_4:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

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

Substance	ΔH_f
CH_4	-74.80 kJ
O_2	0 kJ
CO_2	-393.50 kJ
H_2O	-285.83 kJ

$$\Delta H_{rxn} = [-393.50\text{kJ} + 2(-285.83\text{kJ})] - [-74.80\text{kJ}]$$

$$\Delta H_{rxn} = -890.36\ \text{kJ}$$

HEAT OF REACTION EXAMPLES

- Using the standard enthalpy change values at 25 °C in Appendix Four, determine the standard enthalpy change at 25 °C for the following reaction (the combustion of one mole of propane, which is used with many outdoor grills):

$$C_3H_8\ (g) + 5\ O_2\ (g) \rightarrow 4\ H_2O\ (l) + 3\ CO_2\ (g)$$

Substance and State	ΔH_f in kJ/mol
C_3H_8	-104
CO_2	-393.5
H_2O (g)	-242
H_2O (l)	-286
O_2	0

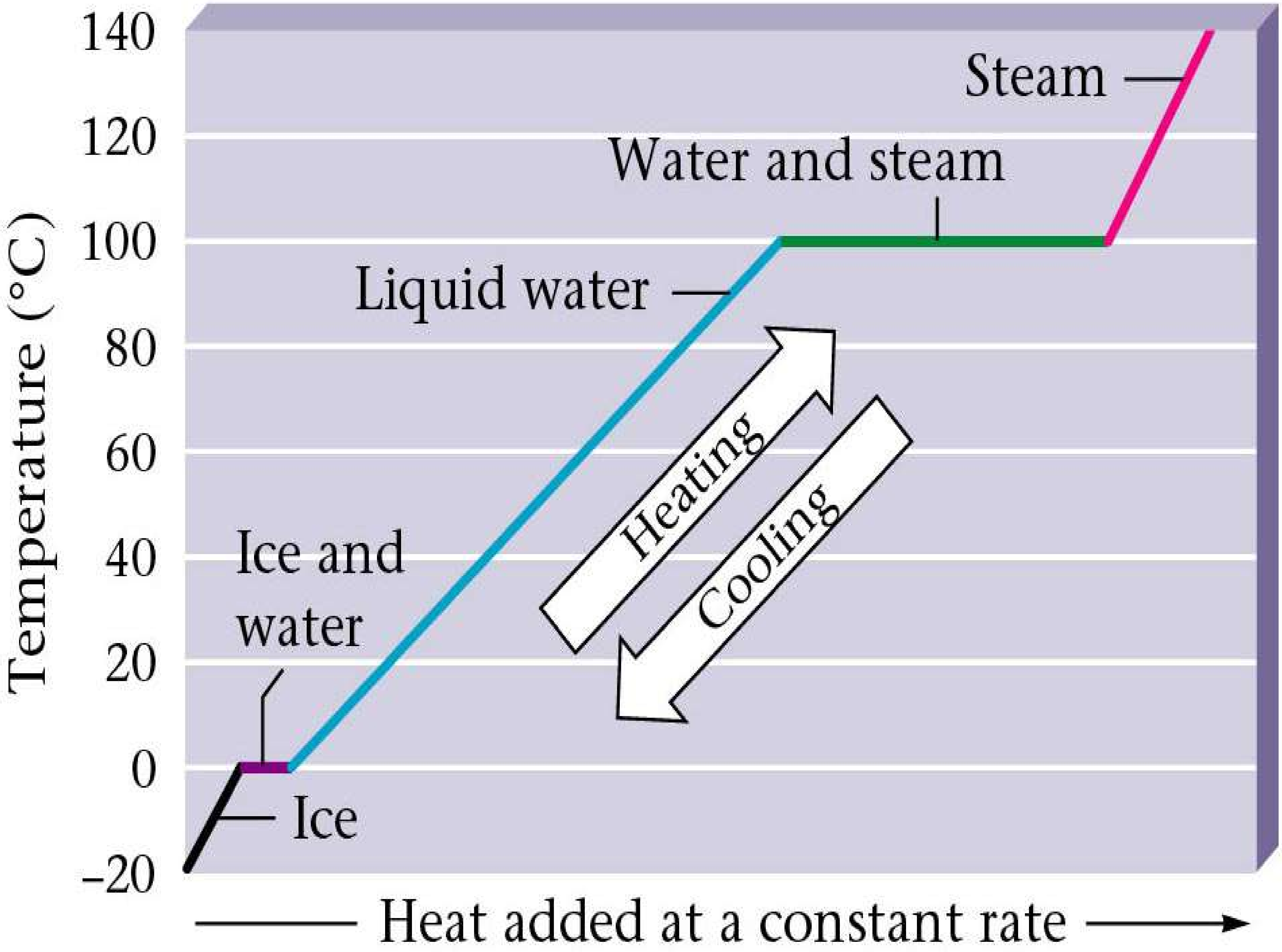
HEAT OF REACTION EXAMPLES

#74. The standard enthalpy of combustion of ethene gas, $C_2H_{4(g)}$, is -1411.1 kJ/mol at 298K. Given the following enthalpies of formation, calculate ΔH_f for $C_2H_{4(g)}$.

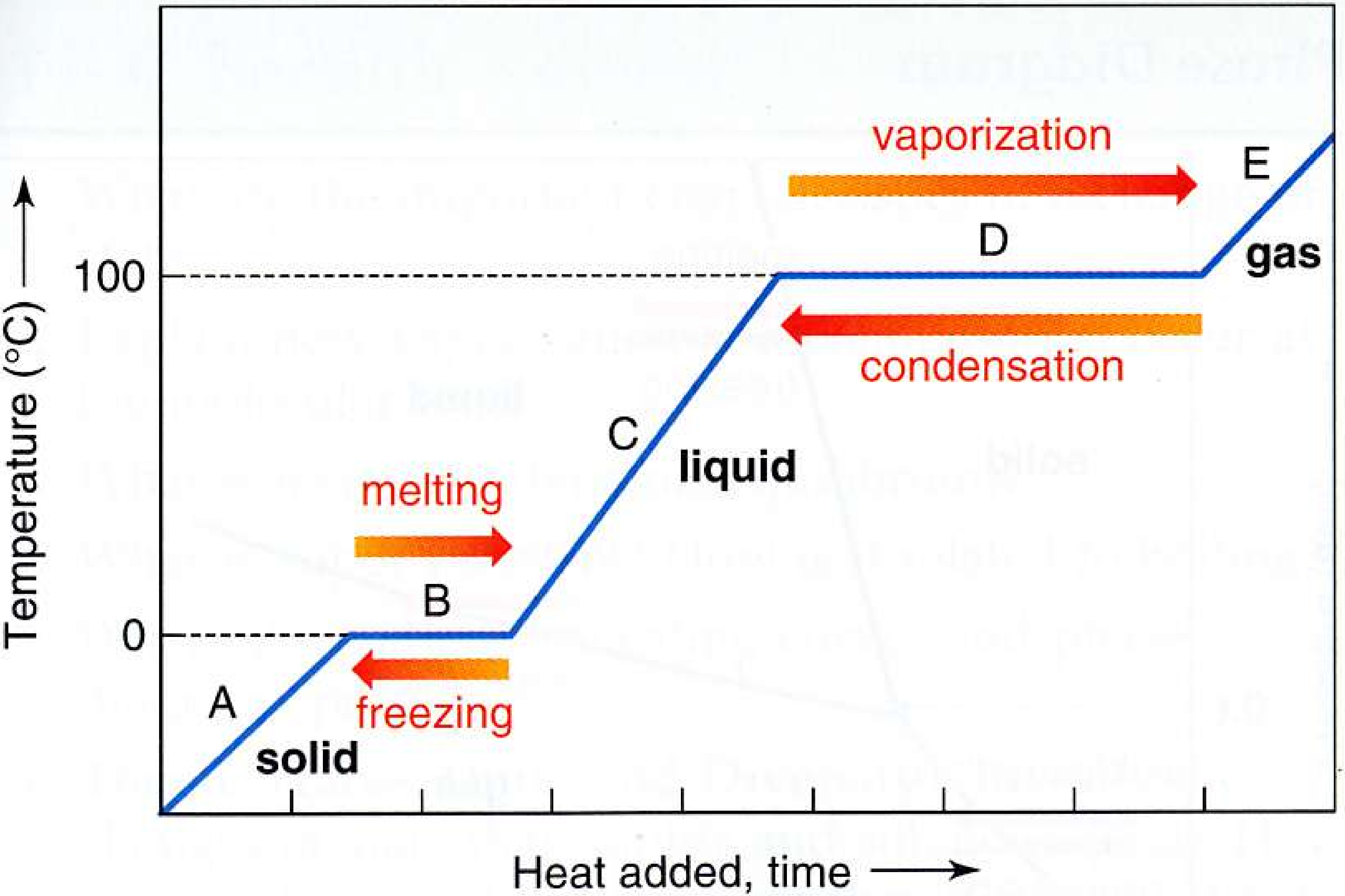
$CO_{2(g)}$-393.5 kJ/mol

$H_2O_{(l)}$-285.8 kJ/mol

HW: 67,68,71,73


140
120
100
80
60
40
20
0
–20
Temperature (°C)
Heat added at a constant rate
Steam
Water and steam
Liquid water
Heating
Cooling
Ice and water
Ice

Heating Curve



FUSION / SOLIDIFICATION

- The heat absorbed by one mole of a substance in melting is the molar heat of fusion (ΔH_{fusion}).
- The heat lost when one mole of a substance solidifies is the molar heat of solidification (ΔH_{solid}).
- $\Delta H_{fusion} = -\Delta H_{solid}$

HEAT CAUSING PHASE CHANGE

- The formula to calculate the amount of energy released or absorbed during a **phase change** is as follows:
- $q = \Delta H_{\text{fusion}} \times \text{mass}$

PRACTICE PROBLEM

- How much energy is required to melt 25.0 grams of ice? Heat of fusion of water is 334 J/g
- 8,350 J

PRACTICE PROBLEM

- How much heat must be removed to freeze a tray of ice cubes if the water has a mass of 50.0 grams?
- - 16,700 J

VAPORIZATION / CONDENSATION

- The amount of heat needed to vaporize one mole of a given liquid is the molar heat of vaporization (ΔHvap).
- The amount of heat released when one mole of gas condenses is called the molar heat of condensation (ΔHcon).
- $\Delta H\ vap = -\Delta H\ con$

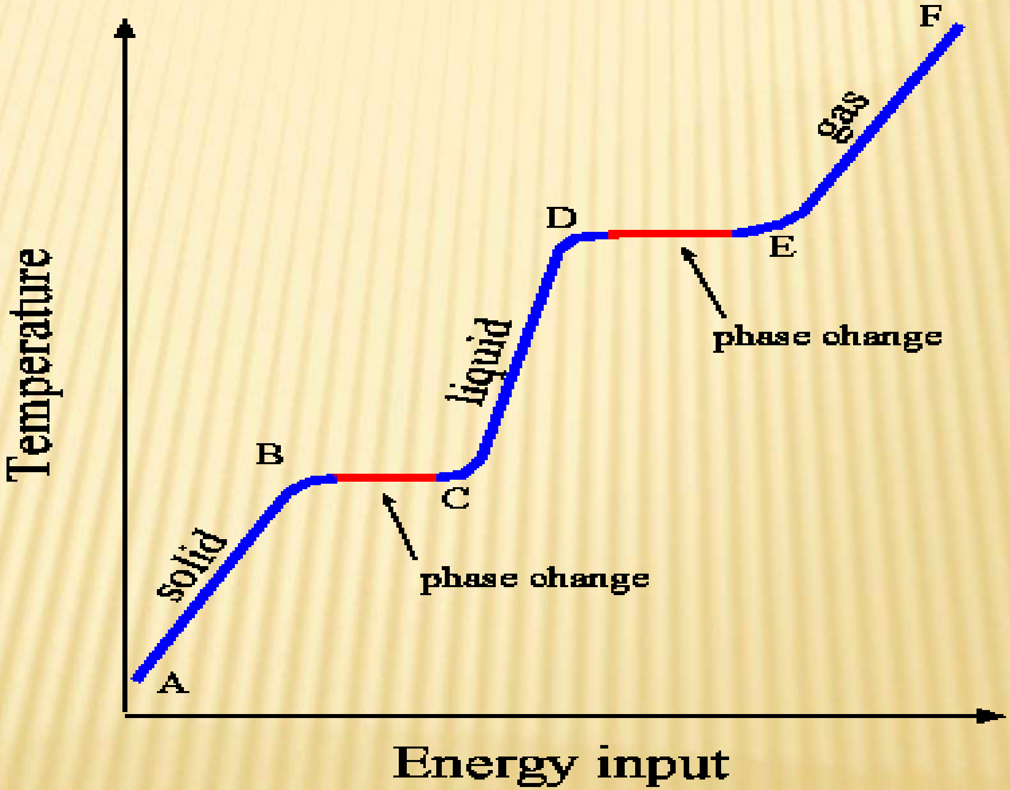
PRACTICE PROBLEM

- How many kiloJoules of energy are released when 24.8 g of water vapor at 100 °C is converted to water at 100 °C? Heat of vaporization of water is 2260 J/g.
- -56,048J or -56.0 kJ.

PRACTICE PROBLEM

- How many kiloJoules of heat are required to vaporize 50.0 g of ethanol, C_2H_5OH? The heat of vaporization for ethanol is 43.5 kJ/mol.
- 47.3 kJ.

PHASE CHANGE GRAPH



THE END

- A 150.0g sample of a metal at 75.0°C is added to 150.0g of H_2O at 15.0oC. The temperature of the water rises to 18.3°C. Calculate the specific heat capacity of the metal, assuming that all the heat lost by the metal is gained by the water. 0.25
- What information would you need to be able to calculate the molar heat capacity of the metal?