Thermochemistry

The study of energy transfers and chemical driving forces

HEAT FLOW

Heat flowing into or out of a system always results in some kind of change to the system

1. The temperature of the system could change
2. There could be some other change, like a change in physical state, for instance

HEAT FLOW

- When heat flowing into or out of a substance results in a ΔT, we can calculate the amount of heat with the equation: $q = ms \Delta T$

- But sometimes heat flowing into or out of a substance results in a different kind of change – *without a temperature change*
  - Melting, freezing, chemical reactions, etc.
  - Measured as ΔH – a change in enthalpy

Enthalpy

- Enthalpy (H) $\Rightarrow$ the total E (KE + PE) of a system at constant P
- when a system reacts,
  - $\Delta H = H_{final} - H_{initial}$
- for a chemical reaction:
  - $\Delta H_{rxn} = H_{products} - H_{reactants}$

The only problem is…

- The enthalpy of a system (H) cannot actually be measured
- KE = $^1/_2 mv^2$
  - the velocity of any object is always relative to a *frame of reference*
  - the absolute velocity of the earth *cannot be determined*

But, we do know…

- For an endothermic reaction, ΔH is (+)
- For an exothermic reaction, ΔH is (-)
- so, ΔH is all that is really important, and it can be measured *if we assume all the energy gained or lost is heat*

$$\Delta H = {}^{q}/_{n}$$

At constant pressure

or... $q = n\Delta H$

Measuring ΔH

- Because $\Delta H = q/n$, the heat lost or gained *per mole*, if we can measure the heat lost or gained, we can know the value of ΔH

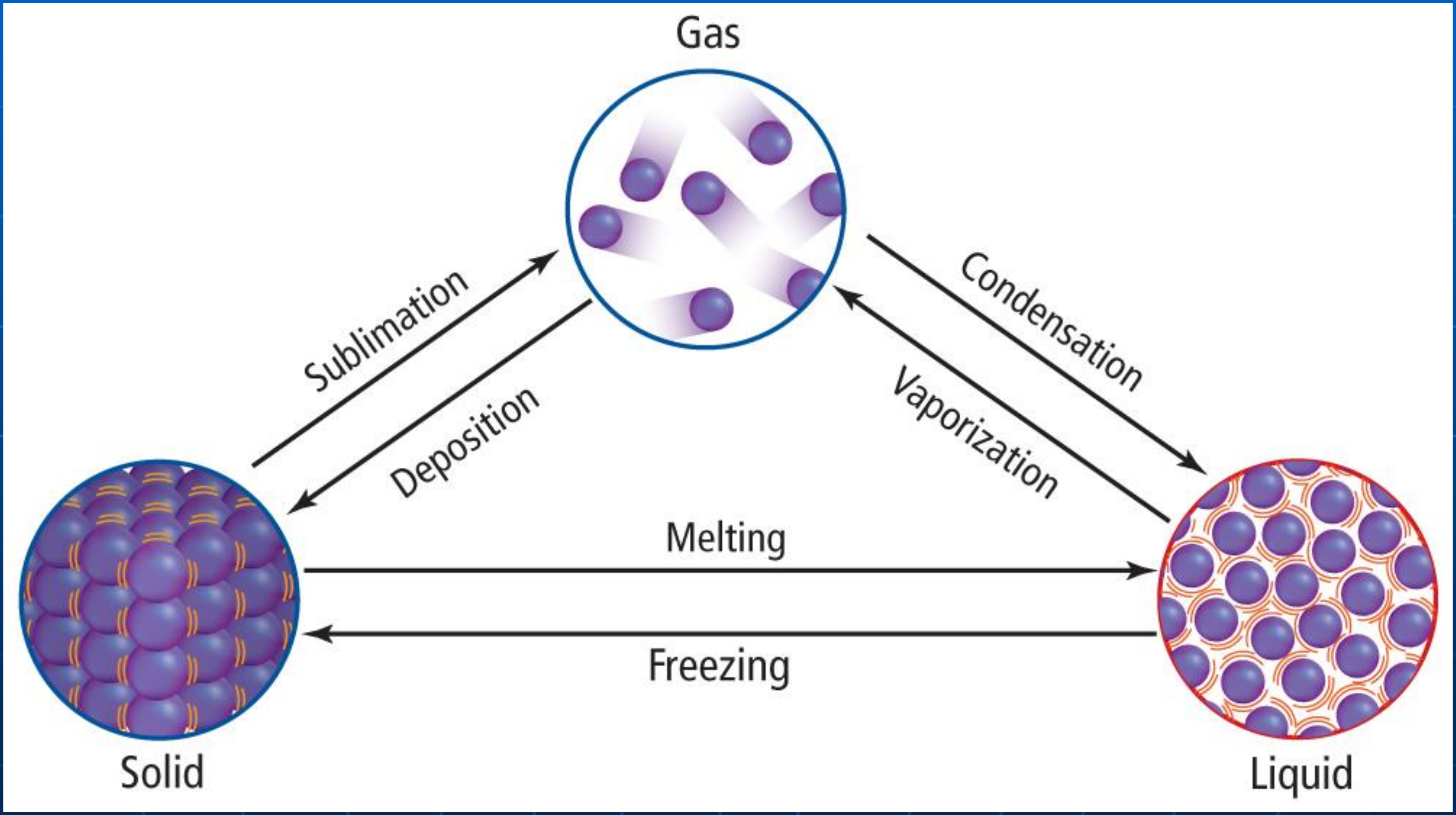
ΔH

- ΔH is a *state function* -
  - that is, what is the absolute difference?
- the "history" of how it got there isn't important
  - ex: T, P, V, etc...

What are all the ΔH's?

- Any energy change for a system that *doesn't result in a ΔT* for the system is measured as *a* ***ΔH***
- Ex: melting/freezing, boiling/condensing, dissolving, or the energy that flows into or out of a reacting system

Changes in state require changes in energy (ΔH)



What do all the ΔH's mean?

- Note:
  - all ΔH's are usually kJ/mol
  - divide the number of kJ of heat that flow by the # of moles
  - reverse process = same #, opposite sign

What do all the ΔH's mean?

- ΔH_{fus} = the heat that must be added to change 1.0mol of a substance from a solid to liquid at it's melting point
- For freezing → use a (-) number
  - *Freezing is exothermic*
- For melting → use a (+) number
  - *Melting is endothermic*

What do all the ΔH's mean?

- ΔH_{vap} = the heat that must be added to change 1.0mol of a substance from a liquid to gas at it's boiling point
- For condensing → use a (-) number
  - *condensing is exothermic*
- For boiling → use a (+) number
  - *boiling is endothermic*

What do all the ΔH's mean?

- **ΔH_{soln}** = the heat that is either absorbed (+ ΔH_{soln}) or released by (- ΔH_{soln}) a substance when it dissolves

- **ΔH_{rxn}** = the heat that is either absorbed (+ ΔH_{rxn}) or released by (- ΔH_{rxn}) the reactants during the course of a chemical reaction

Which ΔH when?

- ΔH_{fus} = melting (+) or freezing (-)
- ΔH_{vap} = boiling (+) or condensing (-)
- ΔH_{soln} = dissolving: can be (+) or (-)
- ΔH_{rxn} = reacting: can be (+) or (-)

To Review: Heat flow can result in several things…

1) If the heat flow results in a ΔT, the equation used is:

$$q = ms\,\Delta T$$

2) IF the heat flow results in a different change – like melting or freezing, the equation is:

$$q = n\Delta H$$

Thermochemistry

The study of energy transfers and chemical driving forces

calorimetry

- A *calorimeter* is a device used to measure the ΔT for a reacting system
- Often, filled with water to absorb or release heat
- The apparatus (and any water within in) are part of the **SURROUNDINGS**

- Because the heat is absorbed by or released mostly from the water, and a bit from the calorimeter, *measuring ΔT of the water allows one to measure q for the reaction*

Heat <u>out of system</u> = Heat <u>into surroundings</u>

$$q_{rxn} = -(q_{H2O} + q_{cal})$$

$$q_{rxn} = -(ms\Delta T + C\Delta T)$$