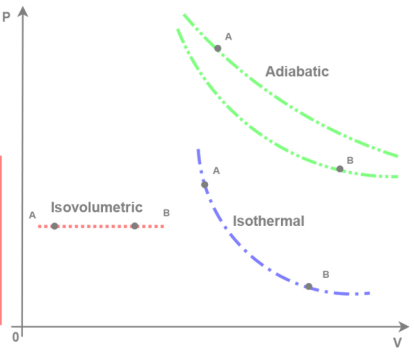
Thermodynamics

States, Systems, Processes

Consider states and state processes in terms of the Ideal Gas Law:

PV = nRT

- This would include considering pressure vs volume graphs
- Work would be calculated as area under the curve
- Adiabatic: P=C/V
- Isovolumetric: NA
- Isothermal: P=nRT/V



Adiabatic: U = -W

Isothermal: U = Q

Isovolumetric: Q = -W

Newton's 1st Law: ΔU = Q – W

(Change in internal energy = heat added into system – work done by system)

Systems:

- **Isolated**: no matter or energy exchange (bomb calorimeters)
- **Closed**: Energy exchange only (radiators)
- **Open**: Energy and matter exchange (an open reaction)

Processes

- **Adiabatic**: no heat exchange, U=
- **Isothermal**: T is constant
- **Isovolumetric**: V is constant=no work
- **Isobaric**: P is constant

States are described by State Functions

Equilibrium usually measured at Standard conditions or Standard Temperature and Pressure (STP)

Standard Conditions: 298 K, 1 atm, 1 M concentrations
STP: 273 K, 1 atm
Conversion: K = °C + 273
Equilibrium conditions will be tested on the MCAT

State Functions

- Pressure (P)
- Density (δ)
- Temperature (T)
- Volume (V)
- Enthalpy (H)
- Internal Energy (U)
- Gibbs Free Energy (G)
- Entropy (S)

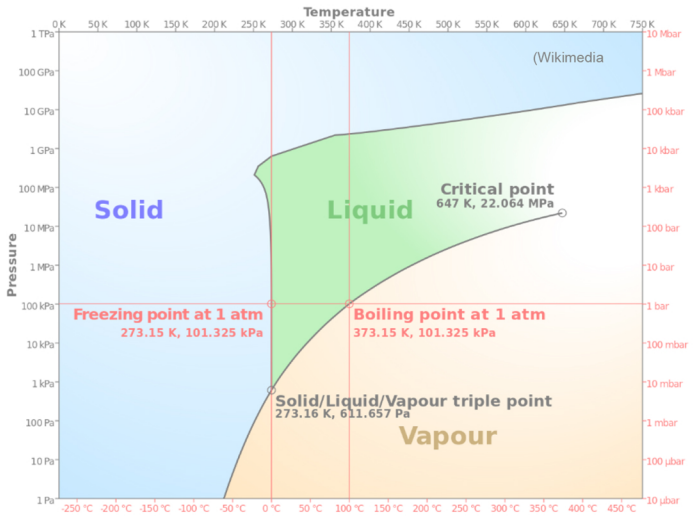
Mnemonic: PAT V. HUGS

Phase Diagrams

Most relevant reactions will take place in standard conditions, so Standard enthalpy, entropy, and free energy values will be used

Terms to remember:

- Melting vs. Freezing (solid ↔ liquid)
- Sublimation vs Deposition (solid ↔ gas)
- Vaporization vs Condensation (liquid ↔ gas)



Phase diagram: https://commons.wikimedia.org/wiki/File:Phase_diagram_of_water_simplified.svg

Heat, Enthalpy, Entropy, and Gibbs Free Energy

Heat (Q) -Think of it less as 'temperature' and more as the kinetic energy of molecules. Q>0, Q<0 means energy added or removed from system, respectively

Temperature and heat are both related to the kinetic energy of a substance: heat is the exchange in energy between two substances at different temperatures.

- Heat measured using calorimetry

Convection: Movement in a fluid due to heat transfer, rising of high T fluid and sinking of low T fluid (gas too)

Conduction: Transfer of heat through direct contact

Radiation: Transfer of heat though electromagnetic waves; infrared radiation

Heating Curves—measuring the heat absorbed by a compound as its T rises (may include fusion, vaporization).

Very Important equation: $q = mc\Delta T$

(looks like q = mcat!)

Q (heat) = (mass)(specific heat cal/gK)(change in temperature)

Other Equations:
1cm^3 of H_2O = 1 mL
For all the energy state functions:

- A positive value means energy is added to the system
- Negative value means energy is released from system (and into surroundings)

Q=mL, m=mass, L=latent heat (cal/g)
$\Delta H_{rxn} = \Delta H_{products} - \Delta H_{reactants}$ (kJ/mol)
$\Delta S = Q/T$ (J/mol K)
$\Delta G = \Delta H - T\Delta S$ (J/mol)
$\Delta G_{rxn} = RTlnK_{eq}$
Linear Expansion: $\Delta L = \alpha L \Delta T$ (a lot)

Enthalpy (ΔH) – Total heat of a compound
Usually considered with regards to the formation of chemical compounds or processes with a reaction mechanism. Standard enthalpies will be provided.

Entropy (ΔS) – Measure of disorder, but a more accurate definition is the measure of the dispersion of energy

- **2nd Law of Thermodynamics**: Tot energy in a system never decreases, entropy is spontaneously maximized
- Reactions usually have positive entropy
- $\Delta S_{gases} > \Delta S_{liquids} > \Delta S_{solids}$

Gibbs Free Energy (ΔG) – For the MCAT, this is generally considered a measure of the 'total energy' in a system or product
Very important to determine the spontaneity of a reaction:

(+) ΔG means reaction is nonspontaneous
(—) ΔG means reaction is spontaneous

Very important: spontaneity has no bearing on the kinetics (speed) of a reaction. This can be a pitfall for some of the comprehensive kinetics/thermodynamics questions

ΔG	ΔH	ΔS	Spontaneous?
(+) at low T, (-) at high T	+	+	Yes, at high T
Always (-)	+	-	Never
Always (+)	-	+	Always
(-) at low T, (+) at high T	-	-	Yes, at low T

Key Takeaways: The MCAT tests understanding more than it tests the ability to plug and chug equations

Knowing units and strong dimensional analysis skills will make answering thermo questions a breeze! Many times, the questions and answers will have hints in the form of units or state functions used that will partially answer the question for you.