



Chemistry Lecture 3 – Thermodynamics

Examcrackers MCAT Comprehensive Course, Charles Feng
<http://fenguin.net/mcat> — fenguin@gmail.com — (224) 532-0039

System: Body you're studying. Can be open (M&E), closed (E) or isolated (neither)

Surroundings: Everything else

State function: Properties describing the state of a system, i.e. internal energy, enthalpy, entropy, Gibbs energy, pressure, temperature, volume, etc. (everything except work & heat)

Intensive property: Properties independent of size, i.e. pressure, temperature

Extensive property: Properties proportional to size, i.e. volume, number of moles, mass

Laws of Thermodynamics

- *First law:* $\Delta E = q + w$ (Energy change = heat flow into system + work done on system)
- *Second law:* heat cannot be completely used for work, or entropy always increases
- *Third law:* a pure substance at absolute zero has zero entropy

Heat

- Natural transfer of energy from warm to cold
- *Conduction:* energy transfer through molecular collisions – SLOW
 - Rate of heat flow: $\frac{Q}{t} = kA \frac{T_h - T_c}{L}$, k is thermal conductivity, L is length, A is face area
 - Note if there's multiple slabs the rate will be the same for each slab
- *Convection:* energy transfer through fluid movement – SLOW
- *Radiation:* energy transfer through electromagnetic waves – FAST
 - Darker colors radiate/absorb heat better; light colors reflect heat better

Work

- At constant pressure: $w = P\Delta V$
- If volume stays constant, no work will be done
- You can graph P vs. V , area under graph tells you total work done

Heat Engines

- Hot reservoir supplies heat which creates work, remainder of heat goes into cold reservoir

$$q_h = q_c + w$$

- *Efficiency:* what % of heat supplied by hot reservoir is used for work
- *Maximum efficiency (Carnot efficiency):* $e = 1 - \frac{T_c}{T_h}$

Refrigerators

- Work is used to take away heat from cold reservoir, bringing it to hot reservoir

$$q_c + w = q_h$$

- *Efficiency:* what % of heat brought to hot reservoir needs to be work
- *Maximum efficiency (Carnot efficiency):* $e = 1 - \frac{T_c}{T_h}$



Chemistry Lecture 3 – Thermodynamics

Examcrackers MCAT Comprehensive Course, Charles Feng
<http://fenguin.net/mcat> — fenguin@gmail.com — (224) 532-0039

State Functions

Internal energy U

- Energy present in molecules, i.e. vibrational, translational, electronic
aka heat energy, thermal energy; depends on temperature
- *Closed system*: $\Delta U = q + w$
- *Closed system with no volume change*: $\Delta U = q$

Temperature T

- Depends on average kinetic energy of molecules
- For each molecule: $KE_{avg} = \frac{3}{2}kT$
- Always convert to Kelvin when you see it in a problem

Pressure P

- KE of molecules causes them to bounce off/exert force on walls of container

Enthalpy H

- Capacity of a system to do work
- $H = U + PV$, $\Delta H = \Delta U + P\Delta V$ at constant pressure
- At its *standard state* (1 bar, 25 degrees C) an element has an enthalpy of 0 J/mol
- *Standard enthalpy of formation* ΔH_f° : change in enthalpy of a reaction that creates one mole of compound from elements in standard state.
- *Heat of reaction*: change in enthalpy from reactants to products $\Delta H_{rxn}^\circ = \Delta H_{f,products}^\circ - \Delta H_{f,reactants}^\circ$
 - Remember that ΔH_f° for aA is $a\Delta H_{f,A}^\circ$ so for $aA + bB \rightarrow cC + dD$, $\Delta H_{rxn}^\circ = c\Delta H_{f,C}^\circ + d\Delta H_{f,D}^\circ - a\Delta H_{f,A}^\circ - b\Delta H_{f,B}^\circ$
- *Hess's Law*: You can add up the individual ΔH_{rxn}° for multiple-step reactions.
 - Remember to balance intermediates between reactions; multiply ΔH_{rxn}° by the balancing factor
 - If you reverse a reaction just multiply ΔH_{rxn}° by (-1)
- *Endothermic*: $\Delta H_{rxn}^\circ > 0$; *Exothermic*: $\Delta H_{rxn}^\circ < 0$
- *Reaction coordinate*: graphing energy vs. reaction progress (can calculate ΔH_{rxn}° from it)

Entropy S

- Measure of disorder of a system (more organized = less entropy)
- *Second law of thermodynamics*: $\Delta S_{system} + \Delta S_{surroundings} \geq 0$ for any process
- *Third law of thermodynamics*: pure stuff at absolute zero has zero entropy
- *Equilibrium*: when a reaction has reached maximum entropy

Gibbs Free Energy G:

- Tells us whether a reaction will be spontaneous or not
- *Formula*: $\Delta G = \Delta H - T\Delta S$
- When $\Delta G < 0$, a reaction will be spontaneous.
- When ΔH and ΔS have different sign, ΔG will have the same sign as ΔH
When ΔH and ΔS have same sign, ΔG will depend on temperature