Path vs State Functions

- Work & heat → path functions → depend on path followed by system
- P, V, T, U (and others) → state functions → only depend on state of system
- Amount of work we obtain from energy source can thus be engineered by influencing path
    - form of fuel efficiency
    - in thermodynamics → determine maximum work under given conditions
- Exploit state functions in calorimetry by defining conditions where they equal other (path function) quantities we want to know

Calorimeters, Heat Capacity and Heat

- Cv & Cp almost the same for solids and liquids → often speak just of heat capacity
- For gases, Cp>Cv because some of absorbed energy redirected into PV (expansion) work
    - deltaV = 0 → Cv
    - deltaP = 0 → Cp

Enthalpy of Reaction

- Change in enthalpy, deltaH, can be determined for any chemical process by measuring the heat in or out of a constant pressure calorimeter. It is a state function
- In chemistry heat of reaction and enthalpy of reaction used interchangeably
    - usually mean molar enthalpy change
- Change in enthalpy
    - deltaH(rxn) → sum H(products) – sum H(reactants)
- Enthalpy is a state function, true for every possible reaction or process
    - Vaporisation (liquid → gas)
    - Condensation (gas → liquid)
    - Fusion (solid → liquid)
    - Freezing (liquid → solid)
    - Sublimation (solid → gas)
    - General rule also applies to these phase transitions

Hess's Law

- As enthalpy is state function: deltaH(rxn)=H(products) – H(reactants)
- Can imagine paths for which overall enthalpy change is the same e.g. via atoms
    - $O_3 + NO \rightarrow 4O + 2N \rightarrow O_2 + NO_2$
    - Break 2 O-O bonds and 1 N-O bond
    - Make 2 N-O bonds and 1 O-O bond
    - reactants → atoms; deltaH1; atoms → products; deltaH2
    - Overall deltaH(rxn) = deltaH1 + deltaH2 = deltaH(atomising reactants) – deltaH(atomising products)

Standard Enthalpies of Formation

- Much more reliable approach; conceptually decompose reactants to elements and then recombine to new (product) compounds
    - uses standard enthalpy of formation
        - enthalpy change when a compound is prepared from elements in all their standard states
        - special circle symbol indicated that we are at standard states

    - standard state → state of matter with lowest enthalpy at 298K and 1atm or 1M solution
        - N_2(g), H_2(g), Br_2(g), hg9l), I_2(s), C(graphite)
        - standard enthalpies of formation of wide range of compounds are tabulated
- We can write out entire reaction in terms of enthalpies of formation
- Enthalpy is extensive → proportional to amount of material present

Combustion Reactions

- Exothermic
    - energy required to break oxygen and fuel (reactant) bonds is less than the energy released when the CO_2 and H_2O (product) bonds are formed
    - CO double bond is strong, so is the polar OH single bond compared to C-C, C-H and C-O etc
- Chemical bonds and fuel efficiency
    - Fuels with more weak (less stable) bonds (e.g. hydrocarbons, fats) yield more energy than fuels with fewer weak bonds (e.g. carbohydrates)
    - C-C and C-H are less stable, thus have more energy than CO double bonds and O-H bonds

Petrol or Gasoline (Hydrocarbon) Fuels

- Obtained by refining crude oil with 3-10 C atoms and mixture of saturated and unsaturated
    - combustion reaction is: C_xH_x (g) + $(x + y/4)O_2$(g) → xCO_2(g) + $y/2H_2O$(g or l)
    - max fuel economy is for slightly lean air/fuel mixtures (excess air) → fuel rich mixtures lead to incomplete combustion and emission of unburnt hydrocarbons and CO
- The heat of combustion (e.g. bomb calorimeter) depends on whether the water remains as a gas (as in a car) or condenses to a liquid (higher calorific value)

Fuel Types and Efficiencies

- Calorific value of fuel is its heat of combustion per g as a limiting reagent of O_2
- A fat contains lots of relatively high energy, unstable C-C and C-H bonds → releases lots of energy as it burns
- A carbohydrate contains lots of relatively stable, low energy O-H bonds → releases less energy as it burns

Hydrogen as a Fuel

- Hydrogen combusts according to: H_2(g) + $1/2O_2$(g) → H_2O(g)
- The calorific value is 120kj/g and each kg (496 moles) of H_2 requires 7.9kg (248 moles) of O_2
- Environmental impact: only direct product is water
    - advantage over Co_2 producing carbon-based fuels
    - Petroleum also often produces CO and hyrdocarbons from incomplete combustion and No, N_2O and NO_2 from nitrogen containing groups
    - environmental impact may be upstream where energy is expended, producing H_2 (electrolysis)
- Safety: no toxic by-products, H_2 is explosive and cannot be readily liquefied
- Storage: no ideal solution so far

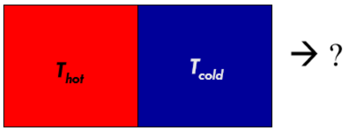
Spontaneous Reactions

- Any reaction will have preferred direction of change: spontaneous in this direction

- At T<0 → water freezing is spontaneous
- At T>0 → water melting is spontaneous
- Most exothermic reactions and some endothermic reactions are spontaneous
    - Sign of deltaH is thus not sole factor in determining spontaneity of reactions

Spontaneous Processes

We are good at recognising spontaneous processes. Eg What happens?



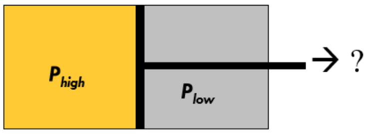
$\Delta U = 0$ for the combined system, or

Heat out of hot body = Heat into cold body

$q_{out} = C_{hot\ body}\ \Delta T = C_{hot\ body}(T_{eq} - T_{hot})$

$q_{in} = C_{cold\ body}\ \Delta T = C_{cold\ body}(T_{eq} - T_{cold})$

$T_{eq} = (C_{cold\ body}T_{cold} + C_{hot\ body}T_{hot})/(C_{cold\ body} + C_{hot\ body})$



$\Delta U = 0$ for the combined system, or

Work done by P_{high} = Work done on P_{low}

$P_{high}\ V_{high}/(P_{eq}\ V_{high,eq}) = P_{low}\ V_{low}/(P_{eq}\ V_{low,eq})$

If total volume = 1, then…

$1/V_{high,eq} = 1 + P_{low}/P_{high}\ (1/V_{high} - 1)$

First Law of Thermodynamics

- Implies that heat can be converted into work and work can be converted into heat, as long as they add up to the same amount → NOT TRUE
- Does not allow us to predict whether a process will occur spontaneously

Second Law of Thermodynamics

- Relates to entropy
- For a process to be spontaneous, the entropy of the universe must increase.
- ΔSsystem + ΔSsurroundings > 0
- (You can only break even at absolute zero).
- Δ = delta/ change in

Third Law of Thermodynamics

- At absolute zero there is only one arrangement of the system (i.e. W = 1), and that is its lowest energy state. A perfect crystal has zero entropy at absolute zero
    - (Absolute zero is unattainable!!)
- The implication of the Third Law is that absolute values can be measured for entropy S. This is not the case for enthalpy H, which can only be expressed as ΔH (delta H)

State Function that Predicts Direction

- Clausius defined state function, entropy (s) in terms of infinitesimal amount of heat that flows reversibly at a particular temperature