Internal Conservation of Energy

- 1st law of thermodynamics: E can't be created nor destroyed
- E changed from 1 form → another (heat → work).

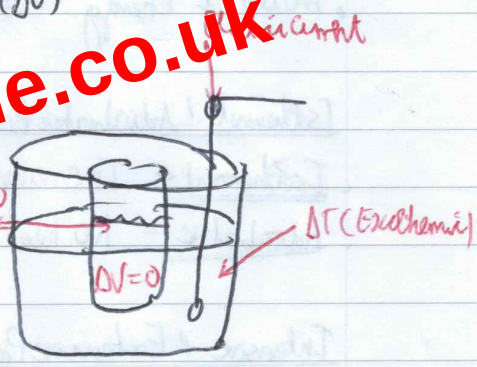
Internal Energy: U

- U = Total Energy = $\sum E_K + E_{vib} + E_{Rotational}$.

For a closed system:

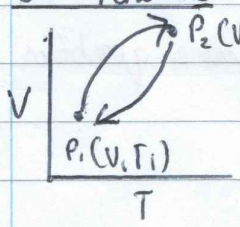
- E given out by system = E gained by surroundings.
- E gained by system = E lost by surroundings.
- E either Heat (q) or Work (w)
- Closed system: change in [$U = \Delta U = q + w$] = heat + work.
- Isolated system: $\Delta U = 0$ ∴ $q + w = 0$
- Absolute value U = undetermined - only measure differences (ΔU)
- Assign E of particular state (Standard state) to 0.

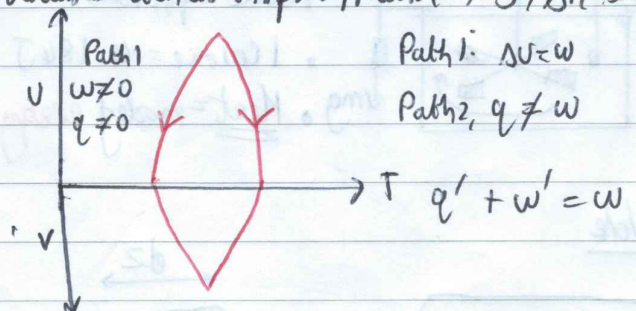
Experimental Measurement of ΔU



- Constant volume adiabatic bomb calorimeter.
- Pressure (Gas in bomb) - Stirred water bath (1) = Calorimeter.
- Temp. from both water baths - @ Same temp.
- No net heat loss from calorimeter to outer water bath - Calorimeter = adiabatic.
- ΔT ∝ q - Releases/absorbs heat; Calibrate calorimeter.
- Burn known mass (Benzoic acid) & measure ΔT → obtain c.

State Functions - Described by variables such as temp. & pressure, V, S, ΔH etc.





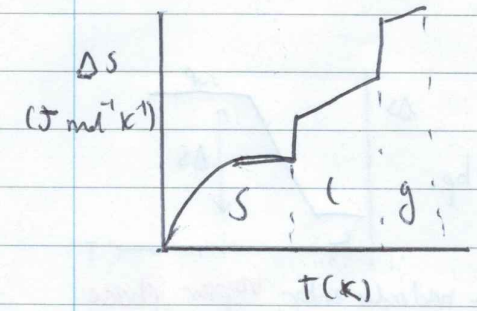
Path 1: ΔU = w
Path 2, q ≠ w
q' + w' = w

- $\Sigma(SF) = \Sigma(SF)_{products} - \Sigma(SF)_{reactants}$.
- ΔU = same for both paths but values of w & w' & q & q' = different.
- Change in state depends only on initial & final states & not on any intermediate conditions.
  - Conservative force.

Boiling Pt & IMFS

Intro

Take a state transition for a substance, e.g Tantalum.



$\Delta G = \Delta H - T\Delta S$

at EQ at same T $\Delta G = 0$, $\Delta H = T\Delta S$

$\therefore \Delta S = \frac{\Delta H}{T}$

- $S \rightleftharpoons l$, $\Delta_{fusion} S = \frac{\Delta_{fusion} H}{T}$
- $l \rightleftharpoons g$ $\Delta_{vap} S = \frac{\Delta_{vap} H}{T}$
- When $\Delta_{fusion} H$ & $\Delta_{vap} H > 0$, heat absorbed from surroundings.
- When $\Delta_{fusion} S$ & $\Delta_{vap} S > 0$ process goes from $S \rightarrow l$ $l \rightarrow g$

Trouton's rule

- For a wide range of liquids, $\Delta_{vap} S = \frac{\Delta_{vap} H}{T} \sim 85\ J mol^{-1} K^{-1}$

Unless compounds with weak IMFs or T H bonding.

- Can be used to estimate $\Delta_{vap} H$ at current T.
- Why? Because high disorder is generated when any liquid evaporates → becomes vapour.
- This disorder = comparable for many liquids.
- Therefore all liquids expected to have similar values of $\Delta_{vap} S^{\ominus}$.

- Liquids that don't obey Trouton's rule do so as they're arranged to be more ordered.
- So ΔS = greater (greater change of disorder) occurs on evaporation
- For H-bonded liquids, H bonds organise molecules so they're less random than others.

Reactions at EQ: Exergonic & Endergonic

- When a reaction has reached EQ ($\Delta G = 0$): $\Delta_r G^\ominus = RT\ln K$.
- Exergonic: $K > 1$ if $\Delta_r G^\ominus < 0$ & $\Delta S^\ominus > 0$; i.e. products in excess $\Rightarrow$ Rxn thermodynamically feasible
- Endergonic: $K < 1$ if $\Delta_r G^\ominus > 0$ & i.e reactants in excess $\Rightarrow$ Rxn Not thermodynamically feasible.

NB: $K \gg 1$ to have significantly more product than reactant.

Conditions when $K > 1$ & $\Delta_r G^\ominus < 0$, Consider $\Delta G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$

1) $\Delta_r H^\ominus < 0$ & $\Delta S^\ominus > 0$, $\Rightarrow \Delta_r G^\ominus < 0$, rxn = Exergonic.
2) $\Delta_r H^\ominus < 0$ & $\Delta S^\ominus < 0$ provided $(T < \Delta H^\ominus / \Delta_r S^\ominus) \Rightarrow \Delta_r G^\ominus < 0$.
3) $\Delta_r H^\ominus > 0$ & $\Delta_r S^\ominus > 0$ provided $(T > \Delta_r H^\ominus / \Delta_r S^\ominus) \Rightarrow \Delta G^\ominus < 0$.
4) $\Delta_r H^\ominus > 0$ & $\Delta_r S^\ominus < 0 \Rightarrow \Delta G^\ominus > 0$ for all temps

E.g For an exergonic (either) reaction:
$KCl(s) \rightarrow K^+(aq) + Cl^-(aq)$ (i.e. dissolution of KCl in water)
$\Delta H^\ominus = +10\ kJmol^{-1}$, $\Delta S^\ominus = 77\ Jmol^{-1}K^{-1}$ @ 298K.

Using 3) above, $298K > \frac{10000\ kJmol^{-1}}{77\ Jmol^{-1}K} = 267.8K$ (THR) $T = \frac{\Delta H^\ominus}{\Delta S^\ominus}$

$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta S^\ominus = 10000 - (298.15 \times 77) = -7\ kJmol^{-1}$

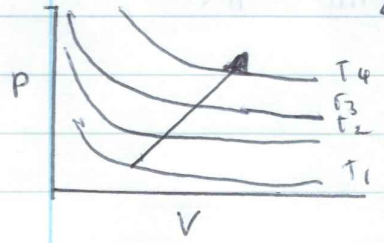
i.e $\Delta G^\ominus < 0$ so this reaction goes!

IMFs & VDW

- Need Ideal Gas Assumptions: V (of molecules) = 0 m^3, no interactions between gas molecules.
- $P = nRT$, $P = \frac{nRT}{V}$, $P \propto \frac{1}{V}$ at T.

- Isotherms show the way P changes with V @ constant T.
- No liquid phase.
- $T_4 > T_3$ etc.

↙ Ideal Gas EQN Isotherms.



Real Gasses

- Atoms / molecules of gas occupy some V, dep
- Attractive & Repulsive interactions exist between gas molecules.
- If this was not true, [illegible] gases (e.g. He)

- We incorporate all this into the VDW Equation

- $P = \frac{nRT}{V}$
  - Introduce a & b as proportionality constants
  - nb = volume of molecules.
  - $\frac{an^2}{V^2}$ = attractive terms proportional to momentum transferred, frequency of collisions.

$\therefore P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$

n = no. of molecules, b = volume of molecules.

Mathematical Tweaks

(i) Undefined = V = nb

(ii) Cubic equation in V: $P = f(V^3, V^2, V, C)$.