Book uses $\underline{\Delta}$ for phase changes and for chemical reactions

ΔH ← change in enthalpy ← change in energy at const P

What we're <u>really</u> interested in (?)

CHEMICAL REACTIONS

We now know that if we ~~[illegible]~~ write:

$$3A + B \rightarrow C + 2D$$

we must specify P, V, and T for each (products & reactants)

At constant pressure, $q_p = \Delta H$

The reactions in a human body produce about 6000 <u>kJ</u>/day (<u>basic</u> metabolic rate).

8,000 - 12,000 kJ/day with activity (exercise, etc)

Remember that you can add or subtract reactions and their corresponding enthalpies

(result of state variables) ↖ Remember from Gen Chem

Temperature Dependence of ΔH

We saw before that to get ΔH for

$$H_2O\ (l \text{ at } 50^\circ) \longrightarrow H_2O\ (g \text{ at } 50^\circ)$$

We could take

$$H_2O\ (l \text{ at } 50^\circ) \xrightarrow{\text{heat}} H_2O\ (l \text{ at } 100^\circ)$$

$$H_2O\ (l \text{ at } 50^\circ) \dashrightarrow H_2O\ (g \text{ at } 50^\circ)$$

$$H_2O\ (l \text{ at } 100^\circ) \xrightarrow{\text{vaporize}} H_2O\ (g \text{ at } 100^\circ)$$

$$H_2O\ (g \text{ at } 100^\circ) \xrightarrow{\text{cool}} H_2O\ (g \text{ at } 50^\circ)$$

Similarly, if we know ΔH for $A \rightarrow B$ at 25° to calculate ΔH for $A \rightarrow B$ at 37°

$$A\ (37^\circ) \xrightarrow[C_p^{(A)}]{\text{Cool}} A\ (25^\circ) \xrightarrow[\Delta H^{25^\circ}_{RXN}]{\text{RXN}} B\ (25^\circ) \xrightarrow[C_p^{(B)}]{\text{Heat}} B\ (37^\circ)$$

(This assumes that $C_p^{(A)}$ and $C_p^{(B)}$ are independent of T over range of $25^\circ \leftrightarrow 37^\circ$)

We never care about H, but only $\underline{\Delta H}$.

Convention has that H = 0 for any/all <u>pure elements</u> in their most stable states at 1 atm

<u>Standard enthalpy for molecules is:</u>
the enthalpy of formation of 1 mol of the compound at 1 atm <u>from</u> it's component elements at 1 atm (H = 0 for each of them)

Standard state → ΔH_f° ← formation

We saw in Gen Chem that we can use standard enthalpies of formation of all components of a reaction to get ΔH for the net reaction.

SUMMARY

1) Heat (q) and Work (w) are exchanges of energy between system and surroundings

2) Chemical reactions or phase changes also change the energy of the system (converting chemical energy).
Intermolecular interactions have <u>energy</u>
Bonds ~~can~~ have <u>energy</u>.

$A \rightarrow B$ if $\Delta H < 0$ System will release energy to surroundings

(dipeptide)

Calculate ΔH for reacting 1 g solid glycyl glycine with O_2 to form solid urea, CO_2 (g) & H_2O (ℓ) at 25°C, 1 atm (isothermal, isobaric).

$$3\,O_2(g) + C_4H_8N_2O_3(s) \rightarrow CH_4N_2O(s) + 3CO_2(g) + 2H_2O$$

$$\Delta H^\circ_{RXN} = \bar{H}^\circ(\text{urea}, s) + 3\bar{H}^\circ(CO_2, g) + 2\bar{H}^\circ(H_2O, \ell) - \bar{H}^\circ(C_4H_8N_2O_3, s) - 3\bar{H}^\circ(O_2, g)$$

Note: $\bar{H}^\circ = \Delta H^\circ_f$

$$= -333.17\ \text{kJ/mol} + 3(-393.51\ \text{kJ/mol}) + 2(-285.83\ \text{kJ/mol}) - (-745.25\ \text{kJ/mol}) - 3(0)$$

$$= -1340.11\ \text{kJ/mol}$$

Heat is taken from system ie. is given off

then $(-1340.11\ \text{kJ/mol})\left(\frac{\text{mol}}{132.12\ \text{g}}\right) = -10.14\ \text{kJ g}^{-1}$

What about doing this at a non-standard temp?

$\bar{H}^\circ$ really means $\bar{H}^\circ_{298}$

But from eq. 2.44 $\quad \Delta H(T_2) = \Delta H(T_1) + \Delta C_p(T_2 - T_1)$

↑ Why ΔC_p?

$$\bar{H}^\circ_T = \underbrace{\bar{H}^\circ}_{\text{formation at 298}} + \underbrace{\Delta C_p^\circ (T - 298)}_{\text{then heat/cool the formed compound}}$$

An example of breaking 1 process into 2 steps

What about other pressures?

For ideal gases, H is independent of P
For solids & liquids, H depends weakly on P (usually)

So often can use $\bar{H}^\circ$ at $P \neq 1$ atm.

Bond Dissociation Energies (Enthalpies)

$$A\text{-}B\ (g) \rightarrow A(g) + B(g)$$

Should be measure of energy required to break bond A-B

Used in Organic texts to get a ~~feel~~ feel for molecule stability.

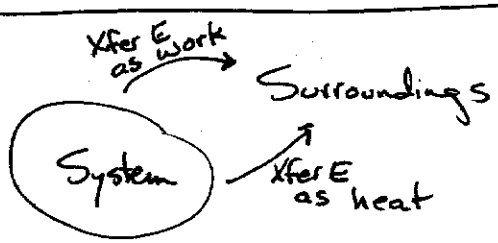
$$CH_3\text{-}H\ (g) \rightarrow \dot{C}H_3\ (g) + H^\cdot\ (g)$$

$$CH_3\text{-}CH_2\text{-}H\ (g) \rightarrow CH_3\text{-}\dot{C}H_2\ (g) + H^\cdot\ (g)$$

} "D" ≈ 415 kJ/mol

ie. for C-H bond generically.
(Not absolute, but often OK...)

SUMMARY:



For an ideal gas, the internal energy is a direct measure of temperature.

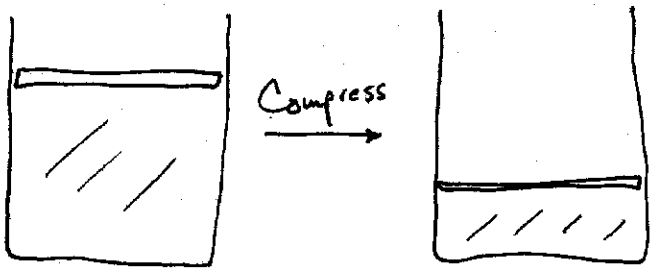
Which is kinetic energy (and rotational and vibrational)

Raise T, raise Kinetic Energy (billiard balls)

Real gases, liquids, solids

↓

translational, rotational, vibrational E's
plus interactions between molecules



We have all the energetic considerations for an ideal gas

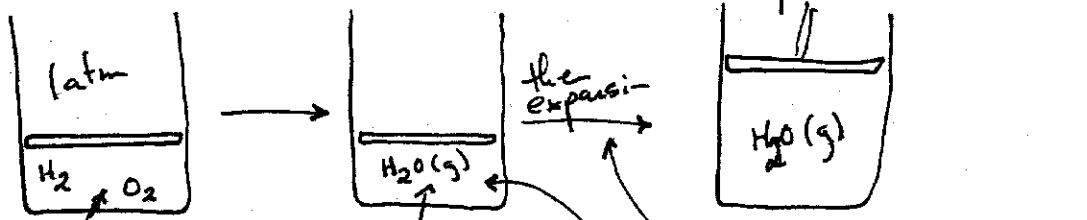
PLUS if the molecules repel each other, we have to put in extra energy to make up for increased repulsion as molecules get closer (on average)

Conversely, if the molecules attract each other, it ought to be easier to compress the gas.

Real heat capacities reflect this.

Chemical reactions (& phase changes) release or absorb large amounts of energy

Auto Engine



Assume for simplicity that the gas in piston is isolated (no heat xfer w/ surroundings – adiabatic)

↑

We know not true – why?

lots of heat liberated. Gas temperature rises dramatically.

Reversible or Irreversible?

Initially, V unchanged
n unchanged

$$P = \frac{nRT}{V} = \left(\frac{nR}{V}\right)_{CONST} T$$

So P increases dramatically.
Pressures no longer balanced,
so volume change!

Less obvious, but cells "carry out" reactions which result in work (electrical, $P\Delta V$, $F \cdot d$, etc.) and heat.

Exercise science and physiologists can tell us all about this!