Mon 9/10/01

Heat Capacity Revisited

C_p = const P
C_v = const V

Heat a solution (or solid, etc) from 35° → 80°C
How much energy (heat transfer) involved?

<u>Const P</u>

$$q_P = \int_{35^\circ C}^{80^\circ C} C_p\,dT \approx C_p \int_{35}^{80} dT$$

$$= C_p\left((80+\cancel{273})-(35+\cancel{273})\right)$$

$$= C_p\,(55\text{K})$$

<u>Aside:</u>

What are units of C?

$$q = \text{energy} = \text{Joules} = \text{J} \Leftrightarrow C_p\,(\text{K})$$

$$\therefore\ C \equiv \text{J/K}$$

$$\left(\text{or } \frac{\text{J}}{\text{K mol}} \text{ for } \bar{C}\right)$$

Now consider a <u>closed</u> system at Constant V

$$w_v = \cancelto{0}{P\Delta V} = 0$$ <u>assuming</u> only PV work

$$\Delta E = q_v + \cancelto{0}{w_v} = q_v$$

How about Constant P?

Define $H = E + PV$ ⇐ Official definition

General for gas, liquid, solid

$\therefore \quad \Delta H = \Delta E + \Delta(PV)$

$= \Delta E + P\Delta V$ (const P)

$= q_p + w_p + P\Delta V$

$(w_p = -P\Delta V)$

Assuming only PV work

$= q_p - P\Delta V + P\Delta V$

$\Delta H = q_p$ ⇐ usual definition

IF NO PV work, $\Delta H \approx \Delta E$

= heat absorbed (heat content)

Phase Changes (require/involve energy)

$H_2O\,(l, 99°C) \rightarrow H_2O\,(l, 100°C) \rightarrow H_2O\,(g, 100°C)$

↑ 75 J input

↑ 40,660 J input

LOTS OF ENERGY — NO TEMP CHANGE

BUT THERE IS A CHANGE

IN TOTAL ENERGY

Reactions — "Heat of reaction" "ΔH"

$\Delta H = q_p$ For many bio systems, pressure is constant, and the volume of the system (liquid solution) doesn't change much.

Endothermic =
heat taken up (*into* the system) $q_p > 0$ "Cools"

Exothermic
heat given off (to surroundings) $q_p < 0$ "Heats"

Remember that E, P, V, T, H are state functions
q and w are *not*.
This only a special case.

At this point, the book recognizes that C is a relatively useless number. $\bar{C}$ *is* useful

Similarly, ΔH expressed *per mole* is the only useful thing here. UNITS ⇒ J/mole

Temperature Dependence of ΔH

$$\Delta H = H\,(\text{products}) - H\,(\text{reactants})$$

Similarly

$$\Delta C_p = C_p\,(\text{products}) - C_p\,(\text{reactants})$$

As before, but now for a reaction $A \rightarrow B$

$$\begin{tikzcd}
A(T_2) \arrow[r, "\Delta H(T_2)"] \arrow[d, "-C_p^A(T_2-T_1)"'] & B(T_2) \\
A(T_1) \arrow[r, "\Delta H(T_1)"] & B(T_1) \arrow[u, "-C_p^B(T_1-T_2) = C_p^B(T_2-T_1)"']
\end{tikzcd}$$

$$\therefore \quad \Delta H(T_2) = -C_p^A(T_2-T_1) + \Delta H(T_1) + C_p^B(T_2-T_1)$$

$$= \Delta H(T_1) + (C_p^B - C_p^A)(T_2 - T_1)$$

$$= \Delta H(T_1) + \Delta C_p^{RXN}(T_2 - T_1)$$

Alternatively $\rightarrow$ $\Delta H = n_B \bar{H}_B - n_A \bar{H}_A = \bar{H}_B - \bar{H}_A$

$$\frac{d\Delta H}{dT} = \frac{d\bar{H}_B}{dT} - \frac{d\bar{H}_A}{dT}$$

$$= \frac{q_p^B}{dT} - \frac{q_p^A}{dT} = C_p^B - C_p^A = \Delta C_p$$

(the book does an analogous, but more complete derivation on p. 51)

Then $$\frac{d\Delta H}{dT} = \Delta C_p$$

$$\int d\Delta H = \int \Delta C_p \, dT$$

$$\Delta H(T_2) - \Delta H(T_1) = \Delta C_p (T_2 - T_1)$$

← IF ΔC_p is independent of T

$$\Delta H(T_2) = \Delta H(T_1) + \Delta C_p (T_2 - T_1)$$

Q ⇒ So, although we sometimes use ΔH as if it's temperature-independent, this only true WHEN ?

Ans: when $\Delta C_p = 0$

Interestingly, $\Delta C_p \gg 0$ for protein folding. So one has to be very careful here.

$U \rightleftharpoons F$
$(A \rightleftharpoons B)$

Also, ΔC_p for transfering a nonpolar molecule from a nonpolar solvent to water is very much non-zero.
We'll see that the behaviour is very similar to protein unfolding (denaturation), and is used as a model both qualitatively and quantitatively.

Heats of Formation ⇒

More from path-independence of state variables.

Review of General Chemistry – look at it!

WHAT DOES IT ALL MEAN? (p. 56)

How do change the $\overset{(\Delta E)}{\text{energy}}$/$\overset{(\Delta H)}{\text{enthalpy}}$ of a system?

1) Heat
2) Work
3) Phase changes
4) Chemical reactions (bonds making/breaking)

Gas – simplest   E directly related T

IDEAL gas ⇒ *no* interactions
⇒ only translational (rotational) kinetic energy is involved.

Real gases, liquids, solids → *inter*molecular interactions

ΔE and ΔH can change *without* change in T

Raising T in a liquid increases kinetic energy, but also increase *Collisions*.
So more ways to "store" added energy
∴ $C_p^{\text{liquids}} > C_p^{\text{gases}}$

Chemical reactions and phase changes
change dramatically the intermolecular
interactions → (and abruptly)

Lots of potential energy in bonds.

Car engines aren't built to run
on temperature changes in a solid,
but by chemical reactions.

... us too!

$\bar{C}_p^{H_2O(l)} = 75$ J/K mol

$\bar{C}_p^{O_2(g)} = 29$ J/K mol

$\bar{C}_p^{H_2(g)} = 29$ J/K mol