

Heat Capacity Revisited

$$C_p = \text{const } P$$

$$C_v = \text{const } V$$

Heat a solution (or solid, etc) from $35^\circ \rightarrow 80^\circ\text{C}$
How much energy (heat transfer) involved?

Const P

$$\begin{aligned} q_p &= \int_{35^\circ\text{C}}^{80^\circ\text{C}} C_p dT \approx C_p \int_{35}^{80} dT \\ &= C_p ((80 + 273) - (35 + 273)) \\ &= C_p (55\text{K}) \end{aligned}$$

Aside:

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 closed system at constant V

$$w_v = P \Delta V \overset{0}{=} 0 \quad \text{assuming only PV work}$$

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

How about Constant P?

General for gas, liquid, solid

Define $H = E + PV$ \Leftarrow official definition

$\circ\circ$

$$\Delta H = \Delta E + \Delta(PV)$$
$$= \Delta E + P\Delta V \quad (\text{const } P)$$

$(w_p = -P\Delta V)$

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

Assuming only PV work

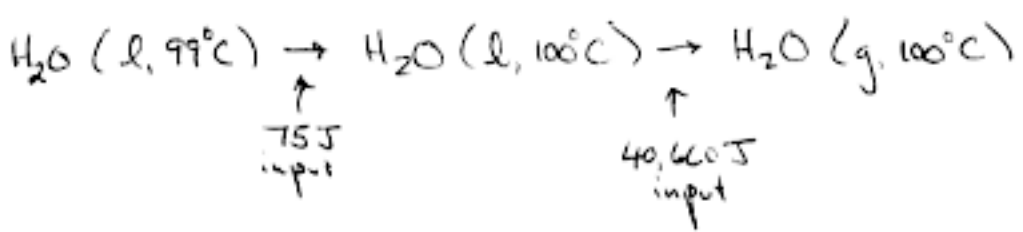
$$= q_p - P\Delta V + P\Delta V$$

$$\Delta H = q_p \Leftarrow \text{usual definition}$$

if NO PV-work, $\Delta H \approx \Delta E$

$$= \text{heat absorbed} \quad (\text{heat content})$$

Phase Changes (require/involve energy)



LOTS OF ENERGY - NO TEMP CHANGE
BUT THERE IS A CHANGE
IN TOTAL ENERGY

Reactions - "Heat of reaction" "ΔH"

→ $\Delta H = \Delta G_P$

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) ~~by~~ $\Delta G_P > 0$ "Cools"

Exothermic heat given off (to surroundings) $\Delta G_P < 0$ "Heats"

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

At this point, the book recognizes that C is a relatively useless number. C is useful

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

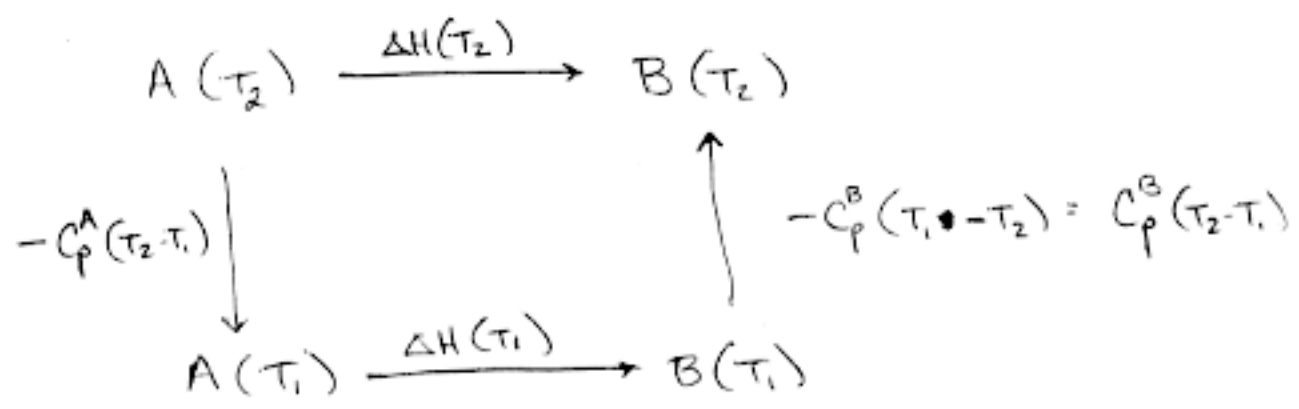
Temperature Dependence of ΔH

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

Similarly

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

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



$$\begin{aligned}
 \therefore \Delta H(T_2) &= -C_p^A(T_2-T_1) + \Delta H(T_1) + C_p^B(T_2-T_1) \\
 &= \Delta H(T_1) + (C_p^B - C_p^A)(T_2 - T_1) \\
 &= \Delta H(T_1) + \Delta C_p^{Rxn}(T_2 - T_1)
 \end{aligned}$$

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

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

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

(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 \Rightarrow 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. \uparrow $U \rightleftharpoons F$ ($A \rightleftharpoons B$)
So one has to be very careful here.

Also, ΔC_p for transferring 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.

(C)

Heats of Formation \Rightarrow

More from path-independence of state variables.

Review of General Chemistry - look at it!

WHAT DOES IT ALL MEAN? (p 50)

How do change the ΔE / ΔH energy/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 \Rightarrow no interactions
 \Rightarrow only translational (rotational)
kinetic energy is involved.

Real gases, liquids, solids \rightarrow intermolecular 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
 $\text{C}_s \rightarrow \text{C}_l \rightarrow \text{C}_g$
solids liquids 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!

$$\bar{C}_p^{\text{H}_2\text{O}(l)} = 75 \text{ J/K mol}$$

$$\bar{C}_p^{\text{O}_2(g)} = 29 \text{ J/K mol}$$

$$\bar{C}_p^{\text{H}_2(g)} = 29 \text{ J/K mol}$$