

The energetic description of a reaction boils down to changing the amount of energy that a system has by doing work on it or adding/removing energy as heat

Some important definitions:

System - the "space" that a reaction is happening in

Surroundings - everything else

U - total internal energy of a system

Endothermic \rightarrow heat transferred TO system $q > 0$

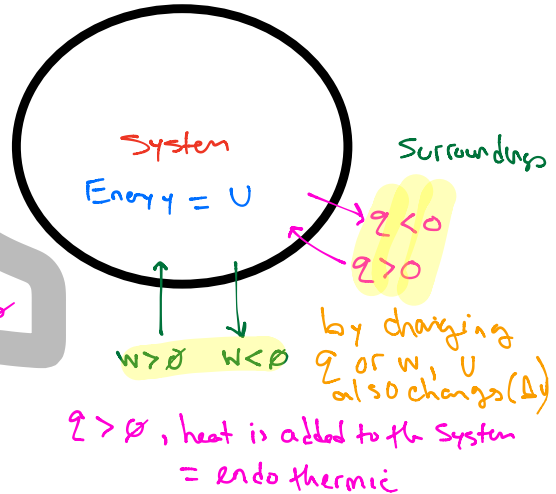
Exothermic \rightarrow heat transferred FROM system $q < 0$

So when a reaction happens, the total internal energy changes

$$\Delta U = U_{\text{final}} - U_{\text{initial}} = w + q$$

remember $\Delta = \text{change}$

The change in energy comes in 2 forms: work and heat



WORK: For chemical and physical changes, work is related to a change in volume

$w = -P\Delta V$ ← remember from gas laws, $P = \frac{\text{energy}}{\text{Volume}}$ so $PV = \text{energy} \rightarrow \text{work} = \text{energy}$

work done by the system

this is the ΔV of the system

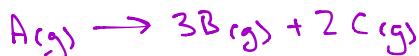
* note that when $\Delta V > 0$, $w > 0$ *

↓
this is an expansion

IF no heat change
so when $\Delta V > 0$, $w < 0$ $\Delta U = w$
 $\Delta U = U_{\text{final}} - U_{\text{initial}}$ $\Delta U < 0$

Think about this as a chemical reaction in the gas phase:

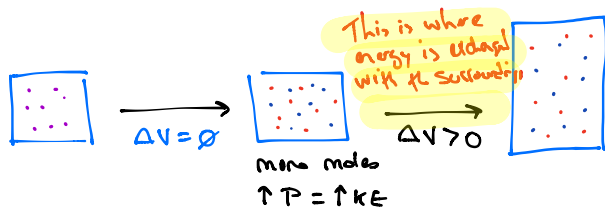
so Energy goes from the system to the surroundings



If T & V are held constant, then the Pressure goes up b/c more moles of gas

If pressure goes up, then the total energy in the container must be higher

Instead of "holding" onto this energy, the system expands (Volume increases)



• During this expansion, the Energy (U) in the system decreases.

- But that Energy went somewhere!

$\Delta U_{\text{system}} < 0$ b/c the system expanded and lost energy

Conservation of energy
- transferred to the surroundings.

$\Delta U_{\text{system}} = -\Delta U_{\text{surroundings}}$ ← again, energy is conserved *1st Law of Thermodynamics*

We can easily calculate this W if we know the pressure and ΔV

How much work is required to compress a gas from 5 L → 2.5 L if the pressure remains constant 1.5 atm? $\Delta V = 2.5 - 5 = -2.5$

Note that 1 L·atm = 101.325 J

→ So work is done ON the system
 $W = -P\Delta V = -1.5 \text{ atm} (-2.5 \text{ L})$

$$W = \frac{-3.8 \text{ L}\cdot\text{atm}}{1 \text{ L}\cdot\text{atm}} \times 101.325 \text{ J}$$

$$W = 380 \text{ J}$$

So how is this related to ΔH , ΔS + ΔG ?

By definition: $H = U + PV$

$\Delta H = \Delta U + P\Delta V$ - assuming no pressure change (this is usually the case because reactions typically happen in open containers, so P_{atm} is constant)

$\Delta U = W + q = -P\Delta V + q$

$\Delta H = -P\Delta V + q + P\Delta V$

$\Delta H = q_P$

← P subscript means constant pressure.

Enthalpy = heat exchange

$q < 0, \Delta H < 0$ = exothermic → Energy (heat) transferred TO the surroundings

$q > 0, \Delta H > 0$ = endothermic → Energy transferred into the system

2nd Law of Thermodynamics: The universe must proceed toward disorder.

$$\Delta S_{univ} > 0$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

ΔG comes from this idea!

Gibbs Free Energy

} Willard Gibbs explained reaction spontaneity with respect to $\Delta H_{sys} + \Delta S_{sys}$

It has origins in thinking about entropy: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = \frac{-\Delta H_{sys}}{T}$$

$$\Delta G = -T\Delta S_{universe}$$

$$\Delta S_{univ} = \frac{-\Delta H_{sys}}{T} + \Delta S_{sys}$$

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

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

This is ΔG → note that $\Delta S_{univ} > 0$ is spontaneous (indeed this a form of the 2nd Law), so $\Delta G < 0$ is spontaneous!

- When $\Delta G < 0$, a process is spontaneous!

If $\Delta G > 0$, $\Delta S_{univ} < 0$

- This can only happen if energy is added to the universe from somewhere else!

3rd Law of Thermodynamics: The entropy of a perfect crystal is zero @ $T = 0$ K.

- This is theoretically impossible

Standard Molar Entropy: S° (this is the value that you can find in the table of formation energies $\Delta G_f^\circ, \Delta H_f^\circ + S^\circ$)

- All matter has disorder $\equiv S^\circ$
- able to make qualitative predictions:

- $S < l < g$ • $O_2(g)$ is more disordered than $O_2(l)$

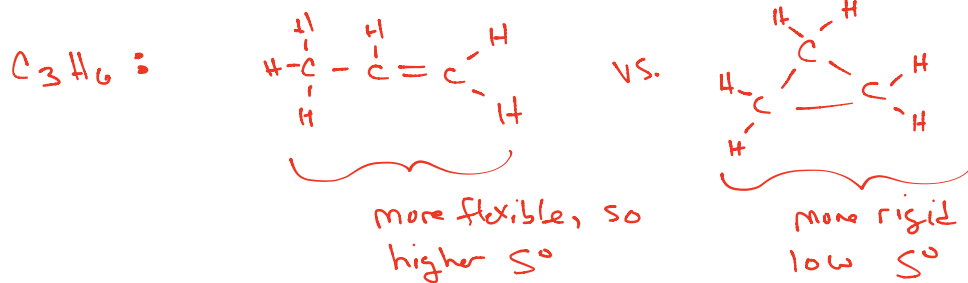
- big molecules store energy (entropy) better than small molecules

• CH_4 is less disordered than C_2H_6

- S° increases with Temperature

• $\text{CH}_4(\text{g})$ at 100 K is more disordered than $\text{CH}_4(\text{g})$ at 50 K

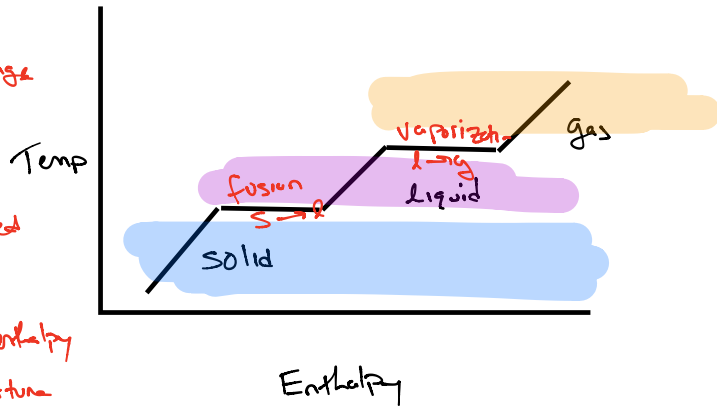
- Molecule structure can influence entropy



Let's think about a similar situation, but this time let's consider enthalpy vs. T

Things to note:

- Temperature does NOT change during a phase change
- During a phase change, the energy that gets added goes to disrupting IMF
- within a given phase, the enthalpy increases with temperature
- moving right on the graph is endothermic ($\Delta H > 0$)
- left is exothermic ($\Delta H < 0$)



Enthalpy is temperature dependent!

$$\Delta H = C_p \Delta T$$

the "p" subscript means constant pressure, which MUST be true. b/c ΔH is q_p

Heat Capacity. This value describes the ability of a substance to absorb energy.

can be presented with units of

$$\frac{J}{g \cdot ^\circ C} \text{ OR } \frac{J}{mol \cdot ^\circ C}$$

ok b/c ΔT in K = ΔT in $^\circ C$

this is Molar Heat Capacity

these values can be found in tables (p. 498 in your book)

How much heat is required to heat 1.97×10^{-2} mol Copper (s) from $28^\circ C$ to $115^\circ C$?

$$C_p = \frac{24.4 J}{mol \cdot K}$$

$$\Delta H \text{ (or } q_p) = n C_p \Delta T = 1.97 \times 10^{-2} \text{ mol} \left(\frac{24.4 J}{mol \cdot K} \right) (115^\circ C - 28^\circ C)$$

$$\Delta H = 39.7 J$$

remember that ΔT is the same in $^\circ C$ + K

will it take more or less to heat the same amount of Na(s) by the same ΔT ?

$$C_p = 28.2 J/mol \cdot K$$

More, b/c C_p for Na $>$ C_p of Cu



BUT - you cannot heat a substance past the temperature that it boils or melts because phase changes take energy!

Sample Problem:

How much energy is required to heat 100 mL H₂O from -17°C to a gas @ 100°C.

$$T_m = 0^\circ\text{C}$$

$$T_b = 100^\circ\text{C}$$

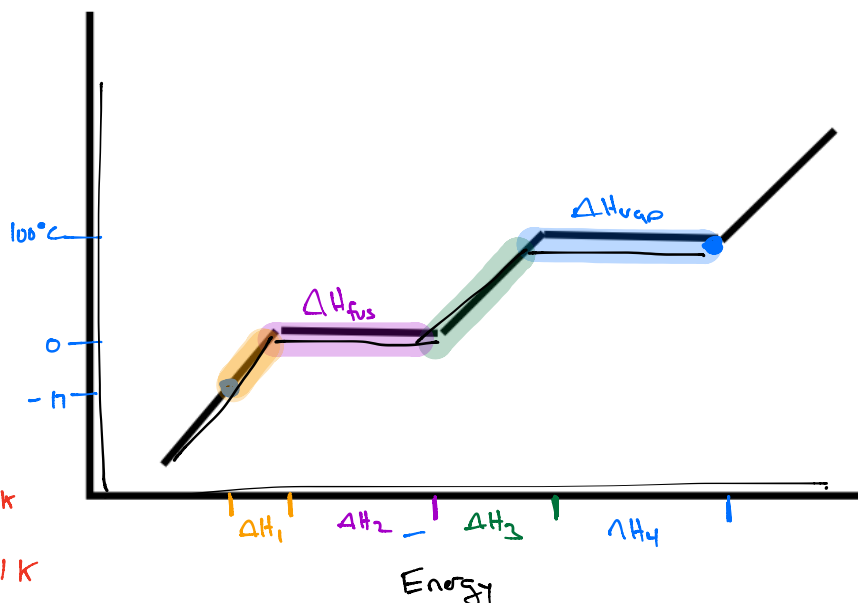
$$\Delta H_{\text{fus}} = 6.01 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta H_{\text{vap}} = 40.65 \frac{\text{kJ}}{\text{mol}}$$

$$C_p \rightarrow \text{solid} = 37.7 \frac{\text{J}}{\text{mol K}}$$

$$C_p \rightarrow \text{liquid} = 75.3 \frac{\text{J}}{\text{mol K}}$$

$$C_p \rightarrow \text{gas} = 33.6 \frac{\text{J}}{\text{mol K}}$$



- ① Always start with the graph above. Label T_m + T_b .
- ② Identify starting + final positions (-17°C + 100°C GAS)
- ③ Identify the path and figure out how many steps. Whenever the slope changes, this is an independent step

$$\textcircled{4} \Delta H_{\text{tot}} = \sum_i \Delta H_n$$

$$\begin{array}{l} \text{density of H}_2\text{O} \\ \downarrow \\ \frac{100 \text{ mL} \cdot 1 \frac{\text{g}}{\text{mL}}}{18.02 \frac{\text{g}}{\text{mol}}} = 5.55 \text{ mol H}_2\text{O} \end{array}$$

$$\Delta H_1 = 5.55 \text{ mol} \left(37.7 \frac{\text{J}}{\text{mol K}} \right) (0 - (-17)) = 3,556.6 \text{ J}$$

$$\Delta H_2 = 6.01 \frac{\text{kJ}}{\text{mol}} \left| \frac{10^3 \text{ J}}{1 \text{ kJ}} \right| (5.55 \text{ mol}) = 33,356 \text{ J}$$

$$\Delta H_3 = 5.55 \text{ mol} \left(75.3 \frac{\text{J}}{\text{mol K}} \right) (100 - 0) = 41,792 \text{ J}$$

$$\Delta H_4 = 40.65 \frac{\text{kJ}}{\text{mol}} \left| \frac{10^3 \text{ J}}{1 \text{ kJ}} \right| (5.55 \text{ mol}) = 225,608 \text{ J}$$

$$\Delta H_{\text{tot}} = 3556 + 33356 + 41792 + 225608 = 304,312 \text{ J} = 304.3 \text{ kJ}$$

Calculate ΔS_{fusion} $\text{H}_2\text{O}(s) \rightleftharpoons \text{H}_2\text{O}(l)$ $T = 0^\circ\text{C}$ (273.15 K)

@ T_m , $\Delta G = 0$ (solid & liquid is @ Equilibrium)

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

$$0 = \Delta H_{\text{fus}} - T_m \Delta S_{\text{fus}}$$

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_m} = \frac{6.01 \text{ kJ/mol}}{273.15 \text{ K}} = 0.022 \frac{\text{kJ}}{\text{mol}\cdot\text{K}} = 22 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$