

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 $q > 0$

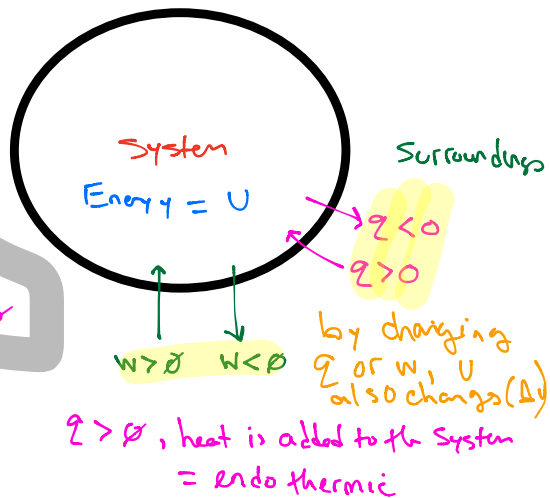
Exothermic \rightarrow heat transferred FROM system $q < 0$

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

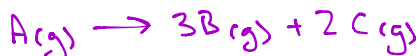
* note that when $\Delta V > 0$, $w > 0$ *

↓
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:

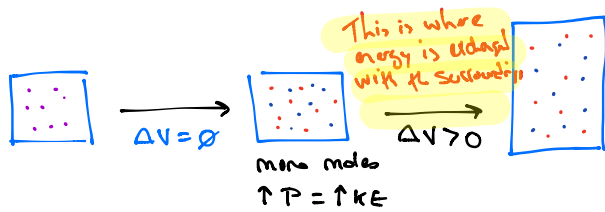
so Energy goes from the system to the surroundings



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

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

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

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

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

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

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

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!

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 $\text{CH}_4(\text{g})$ @ 50 K

- Molecule structure can influence entropy

