

THERMODYNAMICS

AP CHEMISTRY

UNIT 11



LEARNING OBJECTIVES - BE ABLE TO EXPLAIN, USE, CALCULATE, APPLY , & ANALYZE

- Kinetics vs Thermodynamics (speed does not equal spontaneous)
- Enthalpy (H), Entropy (S), and Gibbs free energy (G) (meaning, uses and calculations)
- Wither Reactions that are thermodynamically favorable!!
 - (exo vs endo thermally and more or less disorder)
- Gibbs free energy as it relates to equilibrium

THERMODYNAMIC INTRO

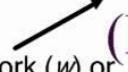
Thermodynamics can tell us direction of a process but not the speed. It does not require knowledge of the pathway. Just Reactants and Products.

- The rate of reaction (speed) is **Kinetics**

1st Law of Thermodynamics: Energy cannot be created or destroyed, Just changes forms

So, with chemical reactions - energy before and after reactions are the same. The reaction might give off energy (**exo**) or absorb energy (**endo**) (Unit 4)

THE TOTAL ENERGY CONTAINED IN A SYSTEM IS
DEFINED BY

Energy, work, & heat

(E) (w) (q)
the ability to do work (w) or produce heat (q)

$$\Delta E = w + q$$

+ w = work is done ON the system (compression)
- w = work is done BY the system (expansion)

+ q = heat is absorbed
- q = heat is released

$$w = -P\Delta V$$

Compression: $-\Delta V$ decreases, $+w$ Work done on system

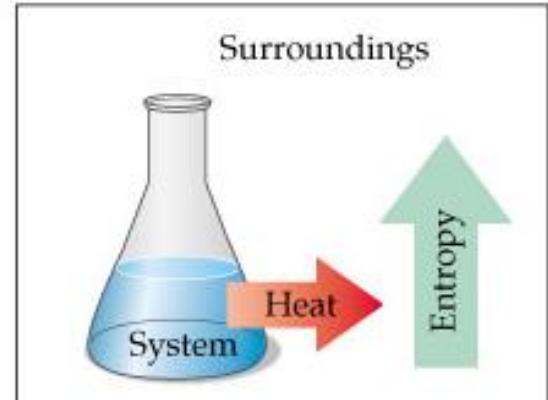
Expansion : $+\Delta V$ increases, $-w$ Work done by system

ENTHALPY (H) REVIEW

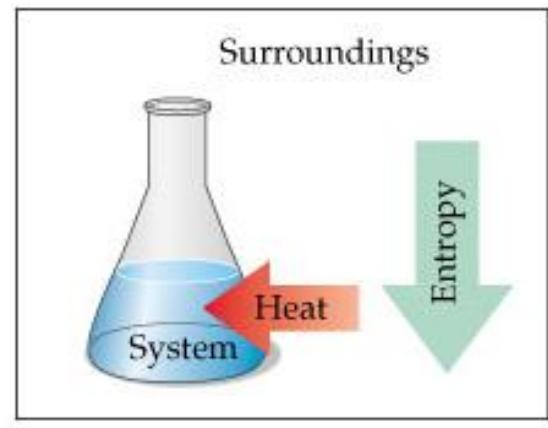
- The flow of energy (heat exchange) in a chemical reaction.
 - You can't say how much heat an object has - but you can measure the transfer of it.
- Hess's Law:
 - The sum of the difference products/mole to reactants/mole

The “Big Mamma” Equation: $\Delta H_{rxn} = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$

(Also known as Hess's Law)



(a)

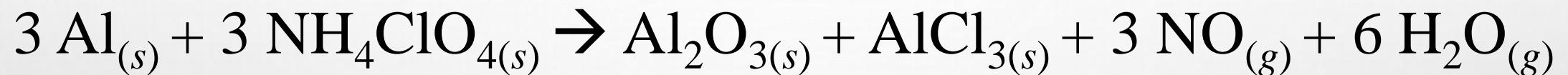


(b)

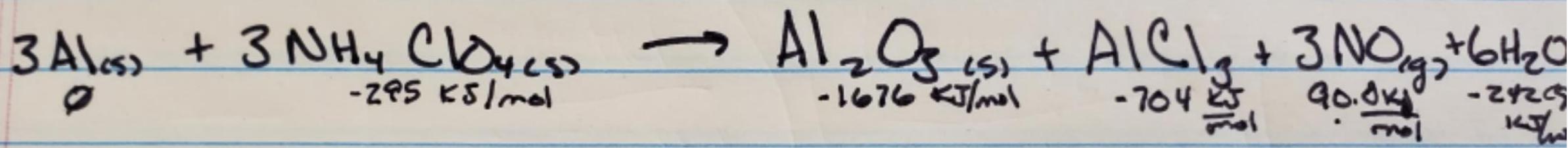
- f —stands for formation. We always assume that forward is favored unless stated or can be determined by the reaction
- Units are KJ/mol_{rxn}

ENTHALPY REVIEW

Given the information below, calculate the $\Delta H^\circ_{\text{rxn}}$ for the following chemical reaction:



<u>Substance</u>	<u>ΔH_f° (kJ/mol)</u>
$\text{NH}_4\text{ClO}_{4(s)}$	-295
$\text{Al}_2\text{O}_{3(s)}$	-1676
$\text{AlCl}_{3(s)}$	-704
$\text{NO}_{(g)}$	90.0
$\text{H}_2\text{O}_{(g)}$	-242



$$\Delta H_{rxn} = \sum \Delta H_f \text{ products} - \sum \Delta H_f \text{ (reactants)}$$

$$\begin{aligned} \Delta H_{rxn} = & \left[\frac{1 \text{ mole}}{\text{mole rxn}} \left(-1676 \frac{\text{kJ}}{\text{mol}} \right) + \frac{1 \text{ mole}}{\text{mole rxn}} \left(-704 \frac{\text{kJ}}{\text{mol}} \right) + \frac{3 \text{ mole}}{\text{mole rxn}} \left(90.0 \frac{\text{kJ}}{\text{mole}} \right) \right. \\ & \left. + \frac{6 \text{ mole}}{\text{mole rxn}} \left(-242 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[\frac{3 \text{ mol}}{\text{mole rxn}} \left(-295 \frac{\text{kJ}}{\text{mol}} \right) \right] \end{aligned}$$

$$= \left[-1676 - 704 + 270 - 1452 \right] - (-885)$$

$\Delta H_{rxn} = -2677 \frac{\text{kJ}}{\text{mol rxn}}$

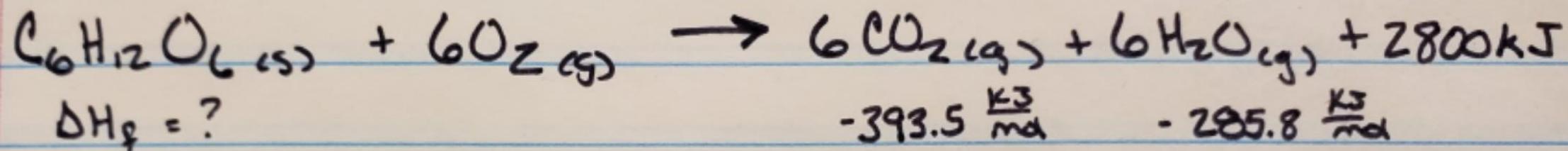
- ∵ Σx0

ENTHALPY REVIEW



Occasionally, not all values are found in the table of thermodynamic data. For most substances it is impossible to go into a lab and directly synthesize a compound from its free elements. The heat of formation for the substance must be calculated by working backwards from its heat of combustion. Calculate the ΔH° formation of $\text{C}_6\text{H}_{12}\text{O}_6(s)$ given the combustion reaction above along with the following information.

<u>Substance</u>	<u>ΔH_f° (kJ/mol)</u>
$\text{CO}_2(g)$	-393.5
$\text{H}_2\text{O}(l)$	-285.8



- ∵ Exo

2

$$-2800 \frac{\text{kJ}}{\text{molrxn}} = \left[\frac{6\text{ mol}}{\text{molrxn}} (-393.5 \frac{\text{kJ}}{\text{mol}}) + \frac{6\text{ mol}}{\text{molrxn}} (-285.8 \frac{\text{kJ}}{\text{mol}}) \right] - H_f_{\text{C}_6\text{H}_{12}\text{O}_6}$$

$$-2800 \frac{\text{kJ}}{\text{molrxn}} = -2361 \frac{\text{kJ}}{\text{molrxn}} - 1714.8 \frac{\text{kJ}}{\text{molrxn}} - \Delta H_f$$

$$\boxed{\Delta H_f_{\text{C}_6\text{H}_{12}\text{O}_6} = -1276 \frac{\text{kJ}}{\text{molrxn}}}$$

A FINAL WORD ON ENTHALPY

Enthalpy is the heat transfer component - it's our endothermic/exothermic marker.

- If a reaction or process releases energy to the surroundings, it's **EXO**thermic.
- If it takes energy in from the surroundings, it's **ENDO**thermic.

It can't be the only factor in determining **if a reaction happens**. Logically, both “cold” and “warm” things happen on their own.

IF a Reaction occurs is one of the Major points of AP Chemistry

There has to be another factor(s). So, let's look at those other Factors

WHAT ARE THE OTHER FACTORS?

Gibbs Free Energy (G) → This is the overall factor that will predict if reaction occurs!!!!

- $\Delta G = \Delta H - T\Delta S$
 - G = Gibbs Free Energy, Units – KJ/ mol_{rxn} (also Kcal/ mol_{rxn})
 - H = Enthalpy, Units – KJ/mol_{rxn}
 - T = Temperature, Units – Kelvin
 - S = Entropy – Units – J/mol_{rxn} · K (2nd Law of Thermodynamics – discuss next)

We use this to predict if a process is **THERMODYNAMICALLY FAVORABLE**

- (old-school term is spontaneous; it's a bit misleading; don't use it).
- If the reaction happens (you witness it), it's thermodynamically favorable (or you can calculate it).
- If it doesn't (or the calculation doesn't support it), it won't

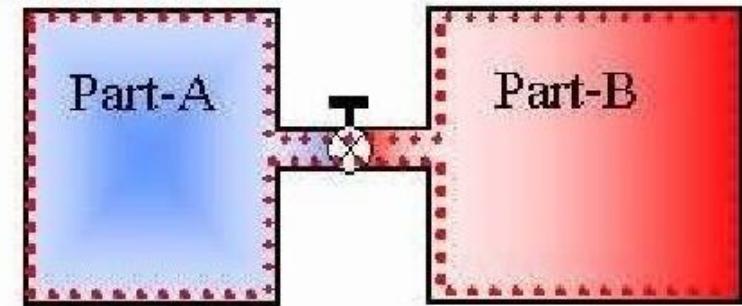
2ND LAW OF THERMODYNAMICS

2nd Law of Thermodynamics:

- Heat can flow spontaneously from a hot object to a cold object:
 - heat will **not** flow spontaneously from a cold object to a hot object
- The **Entropy (S)** of the universe is always increasing
 - Entropy = disorder
- More energy dispersal -> more entropy
- This is a thermodynamic function that describes the number of arrangements that are available to a system at a given state.

What is the 2nd Law of Thermodynamics

Entropy in an isolated system that is not in equilibrium will tend to increase over time until it reaches a maximum equilibrium level



If you keep the door open between two adjoining rooms of different temperatures the cooler room will become warmer and the warmer room will cool down until they both reach the same final temperature

Nature spontaneously proceeds toward the states that have the highest probabilities of existing.

In other words: Nature flows from

- Order → disorder (disorder is favored)
- Low S will change to High S

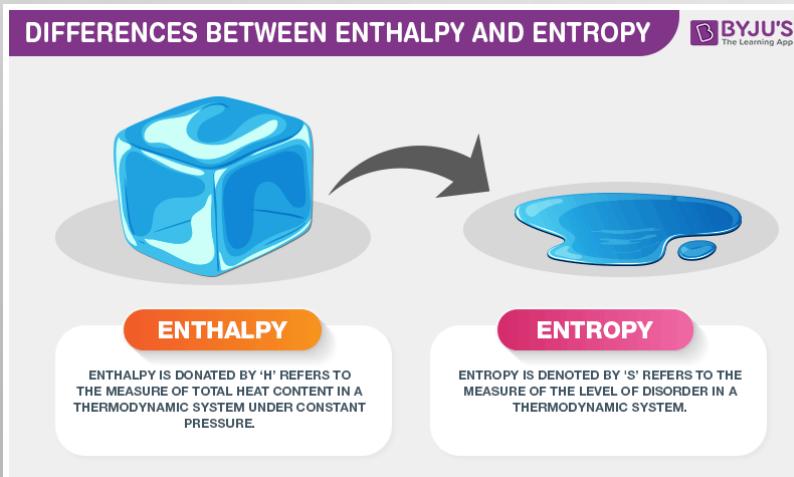
ENTHALPY VS ENTROPY

Enthalpy

- Symbol – H Unit KJ/mole
- First law of Thermodynamics
- Kind of energy

Entropy

- Symbol – S Unit J/(mole · K)
- Second Law of Thermodynamics
- Entropy is a property



Enthalpy vs Entropy

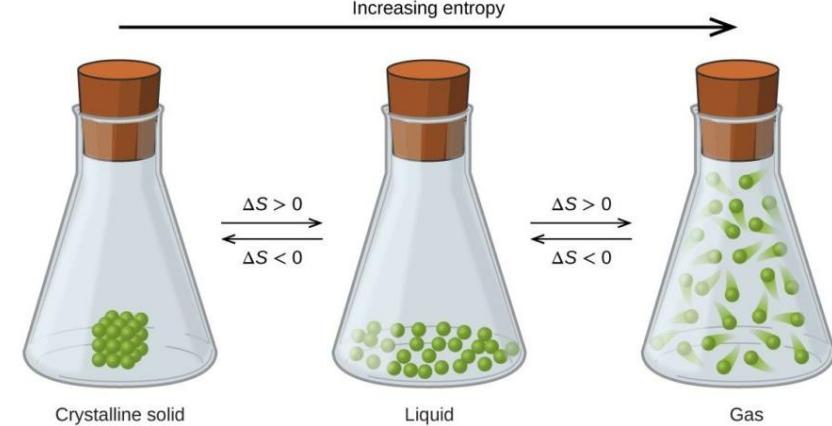
More Information Online WWW.DIFFERENCEBETWEEN.COM

Enthalpy	Entropy
Enthalpy is a thermodynamic quantity equivalent to the total heat content of a system.	Entropy represents the unavailability of a system's thermal energy for conversion into mechanical work.
Gives the heat transfer takes place in constant pressure.	Gives an idea of the randomness of a system.
Relates to the first law of thermodynamics	Relates to the second law of thermodynamics
Can use to measure the change in energy of the system after the reaction.	Can use to measure the degree of disorder of the system after the reaction.

ENTROPY (S)

Positional Entropy (S)

- S increases as a substance changes from a solid to liquid to gas.
- This is because liquid and gaseous states have a higher possibility of shapes and positions (both at the atomic and macroscopic level)
- This is the same for solutions, if we mix two solutions their volumes combine → more volume, more possible shapes or combinations.



Predicting Entropy based on physical evidence:

- When a pure solid/liquid is dissolved, the entropy will increase.
 - Carbonates are the exception
- When gases escape from a solvent (boiling water), entropy increases
- With increasing molecular complexity, entropy increases (KCl vs. $CaCl_2$) More electrons moving...
- Increasing the number of moles of particles increases entropy

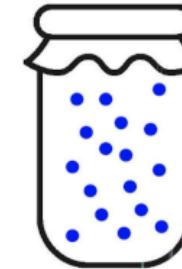
3RD LAW THERMODYNAMICS

Third law – a perfectly crystalline solid at absolute zero has an entropy of zero because this is the MOST ordered state a substance can be ($S=0$)

- Not a measure of energy itself, but how energy is distributed within system it is Enthalpy (H), the thermodynamic quantity that describing the energy of the system
- So Entropy can be determined at any temperature higher than zero K

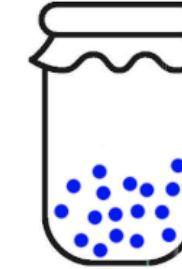
$$\Delta X^\circ_{rxn} = \sum n \Delta X^\circ(\text{products}) - \sum n \Delta X^\circ(\text{reactants})$$

Decrease in temperature



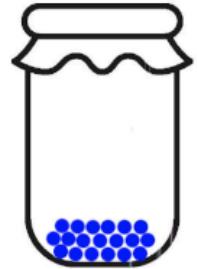
Decrease in kinetic energy

More decrease in temperature



More decrease in kinetic energy

0 K or
-273.15 °C



ZERO kinetic energy

Third Law of Thermodynamics statement:

"The value of entropy of a completely pure crystalline substance is zero at absolute zero temperature"

GIBBS FREE ENERGY

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

Gibbs free Energy:

- Tells if a reaction is thermodynamically favorable
- Indicates the available energy of a substance that can be used in a chemical transformation or reaction
- Entropy and enthalpy interact to describe Gibbs free energy (G)

If ΔG negative, the process is thermodynamically favorable;

if ΔG positive, it isn't favorable.

GIBBS FREE ENERGY

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

Combo #1 → H is negative; S is positive.

- **G will always be negative.** Look at the eqn.
- These reactions are **always thermodynamically favored**
- EXOthermic with greater energy dispersion

Combo #2 → H is negative; S is negative.

- **It depends.** The $(T \times S)$ factor becomes positive.
 - As long as it's small, H wins.
 - So, at **low temperatures**, these still happen
 - So, EXOthermic with less dispersion happens at low temps.

Combo #3 → H is positive; S is positive.

- **It depends again.**
- You need a negative G. Your H factor is positive. Now you need $(T \times S)$ to be big in order to be negative enough to overcome H.
- So, ENDOthermic reactions that create dispersion happen at **HIGH temperatures**.

Combo #4 → H is positive; S is negative.

- **G is ALWAYS positive.**
- **These are never thermodynamically favored.** These won't happen unless you couple them with a process that is TF.

THERMODYNAMICALLY FAVORABLE

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

ΔH	ΔS	T	ΔG	
-	+	Low	-	Always favored
		High	-	
+	-	Low	+	Never favored
		High	+	
+	+	Low	+	Not favored at low temperature Favored at high temperature
		High	-	
-	-	Low	-	Favored at low temperature Not favored at high temperature
		High	+	

Free Energy Change

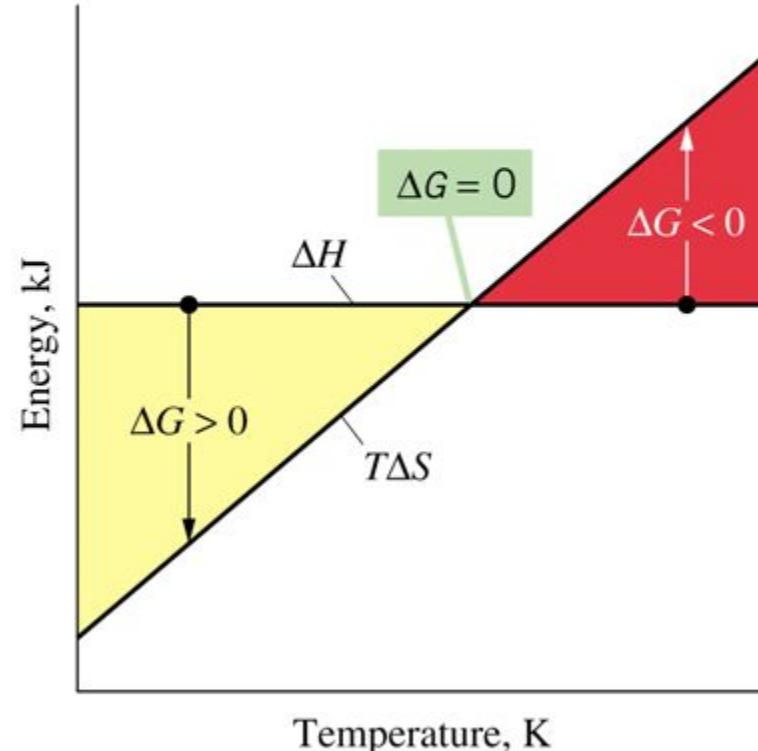
The **free energy change (ΔG)** for a process at constant temperature and pressure is given by the *Gibbs equation*

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

If $\Delta G < 0$ (negative), a process is **spontaneous**.

If $\Delta G > 0$ (positive), a process is **nonspontaneous**.

If $\Delta G = 0$, the process is at **equilibrium**.



Entropy and phase changes

Slow down and think. As you increase temp, the substance ABSORBS energy. So heating a substance is ENDOthermic. But the state goes from less dispersed to more. Solid to liquid and liquid to gas INCREASE entropy.

Removing heat from a substance is EXOthermic, but entropy decreases.

It's odd to think about it, but going from gas to liquid and liquid to solid is less dispersed, but exothermic.

EXTRA REVIEW

BOND ENERGIES

- PREDICTING BOND ENERGIES AND BOILING POINTS
- THIS REQUIRES KNOWLEDGE OF INTRA AND INTERMOLECULAR FORCES.
 - INTRAMOLECULAR FORCE “RANK OF STRONGEST BONDS” (WILL REQUIRE THE MOST ENERGY TO BREAK):
 - IONIC – (+) OR(-) IONS HAVE A TRUE ELECTROSTATIC ATTRACTION THUS HARD TO BREAK
 - OFTEN HAVE LATTICE STRUCTURES WHICH REQUIRE LOTS OF ENERGY TO BREAK
 - COVALENT – IMF'S ARE A “BIG DEAL” WITH THESE
 - DIPOLE – DIPOLE
 - H-BONDING
 - ION-DIPOLE (WILL LEARN MORE LATER)
 - LDF
 - DIPOLE – INDUCED DIPOLE

EXTRA REVIEW

BOND ENERGIES

- YOU CAN'T COMPARE BOILING POINTS AND IMF'S UNLESS THE MOLECULES ARE SIMILAR SIZES.
- BIG VS. SMALL MOLECULES AND BP...
- BONDS ARE NOT BROKEN... IMFS ARE...
- GENERALLY THE MORE POLAR A MOLECULE IS, THE STRONGER THE ATTRACTIVE FORCE BETWEEN MOLECULES ARE.
 - MORE POLAR TYPICALLY REQUIRES MORE ENERGY TO OVER COME IMF'S (ENDO) AND RELEASE MORE ENERGY BY FORMING IMF'S (EXO)

EXTRA REVIEW

Enthalpy	Entropy
It is the sum of internal energy and flows energy	It is the measurement of the randomness of molecules
Enthalpy is a kind of energy	Entropy is a property
It is denoted by symbol H	It is denoted by symbol S
It was termed by a scientist named Heike Kamerlingh Onnes	It was termed by a scientist named Rudolf Clausius
Its unit is Jmol ⁻¹	Its unit is JK ⁻¹
The system favour minimum enthalpy	The system favour maximum entropy
It related is applicable in standard conditions	It does not have any limits or conditions.

Thermodynamics tell us IF a reaction happens.

Kinetics tells us how quickly it happens.

Equilibrium tells us where the endpoints is and where the balance