

# THERMODYNAMICS

-study of energy transformations

Chemical reactions involve not just the conversion of reactants into products, but also involve an energy change- heat. Energy changes accompany all chemical reactions and are due to rearranging of chemical bonding. The energy of chemical bonding (a form of potential energy) should be considered in terms of breaking existing bonds and forming new bonds.

Often, the outcome of an exothermic reaction is a decrease in internal energy, while the outcome of an endothermic reaction is an increase in internal energy.

*Question:* What can happen to a system in which an internal energy change is occurring?

*Answer:* The system can undergo a change in temperature, a phase change can occur, or a chemical reaction can be initiated.

## Heat, Work, and Energy:

*1st Law of Thermodynamics = Law of Conservation of Energy*

In a chemical system, the energy exchanged between a system and its surroundings can be accounted for by heat (q) and work (w).

$$\Delta E = q + w$$

Process	Signs
Work done by the system on the surroundings	-
Work done on the system by the surroundings	+
Heat absorbed by the system from the surroundings (endothermic)	+
Heat absorbed by the surroundings from the system (exothermic)	-

The expansion/contraction of a gas against external pressure:

$$w = -P\Delta V$$

P units would be 101.3 J/L.atm

\*If there is no change in the total volume of gas before/after a reaction occurs, there is no significant work done by or on the system.

Chemicals react at a constant external pressure (often 1 atm). Enthalpy can be considered to be energy with work taken out. Of course,  $\Delta H$  will represent the exchange of heat between a system and its surroundings at constant external pressure.

$$\Delta H = \Delta E + P\Delta V$$

ex. A gas absorbs 28.5 J of heat and then performs 15.2 J of work. The change in internal energy of the gas is:                      Answer ?

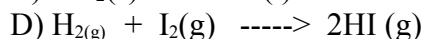
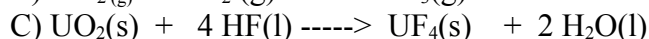
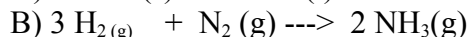
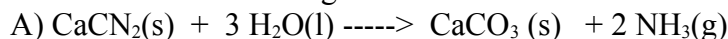
### Constant Conditions:

Here's a list of how the first law behaves when various conditions are held constant.

- Under conditions of constant volume  $\Delta V = 0$ . Since  $W = 0$  and  $\Delta E = q$ .
- When there is no heat flow,  $q=0$  and  $\Delta E = -w$ .
- When the temperature of a gaseous system is constant,  $\Delta E = 0$  and  $q=w$ . Recall that the internal energy is directly proportional to its temperature.
- When the external pressure remains unchanged,  $q$  is referred to as the change in enthalpy. Under these conditions the 1st law may be written as  $\Delta E = \Delta H - P \Delta V$ . In a chemical reaction in which the # of moles of gas is constant,  $\Delta V=0$ , and  $\Delta E = \Delta H$ .

question ----->

In which of the following reactions will the value for  $\Delta E$  be greater than that of  $\Delta H$ ?



answer ---->

$\Delta E = \Delta H - P \Delta V$  is clear that if the value of work  $P \Delta V$  is negative,  $\Delta E$  will be greater than  $\Delta E = \Delta H$ . For any rxn that consumes more moles of gas than it produces the value of  $\Delta V$  will be negative. B is the choice. (produces 2 moles of gas while consuming 4 moles of gas. The final V is less than its initial volume. It results in  $-W$  and a value for  $\Delta E > \Delta H$ .

### ENTHALPY

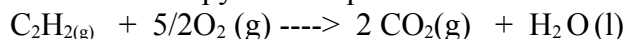
A state function used to describe the heat changes that occur in a reaction under constant pressure. When a reaction is allowed to take place in an open container a quantity of heat proportional to the quantity of matter present, will be released or absorbed.

### Hess's Law

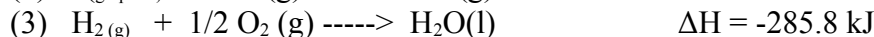
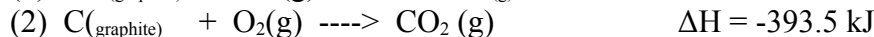
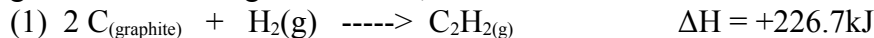
This law states that the enthalpies of reactions may be added when these reactions are added. Substances appearing on the same side are added, while those on opposite sides are subtracted. Some reactions will need to be reversed and multiplied through by a by number, so that when they are combined the desired equation will result.

question ---->

Find the enthalpy of the equation:



given the following information;

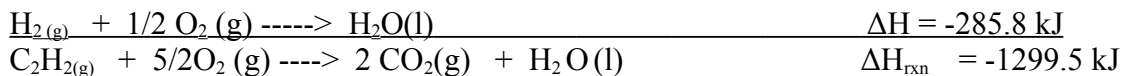


answer --->

Since  $\text{C}_2\text{H}_2(\text{g})$  appears only in equation (1) it is necessary to reverse equation 1 so that the  $\text{C}_2\text{H}_2$  appears on the left hand side to correspond to the desired equation.

Since  $\text{CO}_2(\text{g})$  appears only in equation (2), it is necessary to multiply equation (2) by 2, so that 2  $\text{CO}_2$ 's will appear on the right hand side.

Since H<sub>2</sub>O(l) appears only in equation (3), there is no need to alter this equation since one H<sub>2</sub>O appears on the right hand side of equation (3) and this is exactly what is required in the desired equation.



### What is the difference between the Standard Heat of Formation and Standard Heat of Reaction?

The enthalpy change which occurs when 1 mole of a compound is produced from its elements in their standard heat of formation. When all substances in a chemical reaction are in their standard states, the enthalpy change is called the standard heat of reaction.

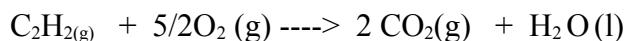
### Bond Dissociation Energy

The change in enthalpy required to break a bond is called the bond dissociation energy ( or bond energy). When bonds are broken energy is absorbed. When bonds are formed energy is released. Here's the equation for the bond dissociation of hydrogen:



\*The larger the bond energy, the greater the bond's strength and the shorter the bond's length. The  $\Delta H_{\text{rxn}}$  can be determined by :  $\Delta H_{\text{rxn}} = [\sum \text{bond E. (reactants)}] - [\sum \text{bond E. (products)}]$

question ----->



C-C	H-C	H-O	C=O	C=C	C≡C	O=O
347	414	464	803	611	837	498

solution ----->

1. Work out the structural formulas to ID the # and types of bonds:



2.  $\Delta H = [2 (\text{H}-\text{C}) + 1 (\text{C}\equiv\text{C}) + 5/2 \text{O}=\text{O}] - 4 [(\text{O}=\text{C}) + 2 (\text{H}-\text{O})]$

3.  $\Delta H = [2(414) + 1(837) + 5/2 (498)] - [4(803) + 2(464)] = -1230\text{kJ}$

\*This method is less accurate than the previous method due to bond energies taken are usually averages.

### **ENTROPY**

It is a quantitative measure of the disorder or randomness of a system. The greater the number of ways that matter can be arranged, the great entropy.

#### Hints:

Entropy increases with temperature

$S < L < G$  for entropy

When the number of moles of gas increase the entropy will increase

When pure substances form mixtures, entropy will increase

$$\Delta S^{\circ}_{\text{rxn}} = [\sum S^{\circ}(\text{products})] - [\sum S^{\circ}(\text{reactants})]$$

Units are: J/K or J/K.mol

2nd Law of Thermodynamics; Any reactions that tends to proceed forward to form products is said to be spontaneous. The total change of entropy will be positive.

$$\Delta S(\text{universe}) = \Delta S \text{ system} + \Delta S \text{ surroundings} > 0$$

\*All isolated systems spontaneously tend toward equilibrium. Once a system reaches equilibrium it achieves a maximum state of entropy.

### GIBBS FREE ENERGY

G is a measure of energy available to the system to do useful work. The difference in free energy between the products and the reactants is the free energy change  $\Delta G$ . It determines the direction of a reaction. However, it is activation energy which determines its rate.

$\Delta G = -$  (reaction is spontaneous)

$\Delta G = +$  (reaction is nonspontaneous)

$\Delta G = 0$  (reaction is equilibrium)

In general, nature likes to move toward two different and contradictory states - low energy and high disorder, so spontaneous processes must result in decreasing enthalpy or increasing entropy or both.

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

Goose Hunters Take Shotguns

OR Gators Hate the Seminoles

T=must be in K

units for energy ( $\Delta H$  &  $\Delta S$ ) = must be same units

$\Delta H$	$\Delta S$	T	$\Delta G$
-	+	low - high -	always spontaneous
+	-	low + high +	never spontaneous
+	+	low + high -	not spontaneous (low T) spontaneous (high T)
-	-	low - high +	spontaneous (low T) not spontaneous (high T)

Note: Since boiling and freezing are equilibrium processes  $\Delta G = 0$ . Setting  $\Delta G = 0$  and solving for temperature in  $\Delta G = \Delta H - T\Delta S$  gives:

$$\text{normal BP} = \frac{\Delta H^{\circ}_{\text{vap}}}{\Delta S^{\circ}_{\text{vap}}}$$

$$\text{normal FP} = \frac{\Delta H^{\circ}_{\text{fus}}}{\Delta S^{\circ}_{\text{fus}}}$$

\*The standard free energy change,  $\Delta G^0$  is defined as the change in free energy which results when all reactants and products are in their standard states and all solutions are at 1 M concentration.

$$\Delta G^0_{\text{rxn}} = [\Sigma G^0(\text{products})] - [\Sigma G^0(\text{reactants})]$$

Another way to find  $\Delta G^0$  is from K (equ constant);

Gases are at 1 atm and the reaction quotient (Q) will be equal to one. If values of K are  $> 1$  will be spontaneous under standard conditions.

$$\Delta G^0 = -2.3 RT \log K$$

If  $K < 1$ ,  $\Delta G^0 > 0$

The rxn will proceed toward the rxts and is nonspontaneous

If  $K = 1$ ,  $\Delta G^0 = 0$

The rxn is already at equilibrium

If  $K > 1$ ,  $\Delta G^0 < 0$

The rxn will proceed toward the products and is spontaneous

To solve for the free energy change under nonstandard condition, you may use the equation below:

$$\Delta G = \Delta G^0 + 2.3 RT \log Q$$

Recall that for the reaction,  $aA + bB \rightleftharpoons cC + dD$

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Note = The units of concentration of gases should be in atm and aq solutions are in M. Pure solids and liquids do not appear in either Q or K.

*Third Law of Thermodynamics- The entropy of a pure perfect crystal at the absolute zero of temperature is 0.*