Notes: Chapter 20

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12:03 AM

## Chapter 20
## Thermodynamics: Entropy, Free Energy, and the Direction of Chemical Reactions

Homework:

Thermodynamics is the study of energy changes within systems. Its principles can be applied equally well to physical and chemical systems.

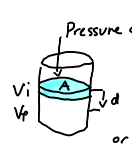
**The First Law of Thermodynamics; Enthalpy**

Energy is conserved between the system and the surroundings; that is, when energy is lost by the system, that same quantity is gained by the surroundings and vise versa. For this reason, the first law of thermodynamics is also called the law of conservation of energy.

When energy is lost by the system, the sign of the energy change is negative. When energy is gained by the system, the sign of the energy change is positive.

The total energy within a system is called the internal energy. The change in internal energy is given by:

$DU = U_{final} - U_{initial}$




$W = F \times D$

$F = -P\Delta V$

or $W = P\Delta V$

**When $\Delta U$ is negative,** we say that the energy change is **exothermic** and energy is lost to the surroundings.

**When $\Delta U$ is positive**, we say that the energy change is **endothermic** and energy is gained by the system.

We can also describe the change in internal energy of a system in terms of the heat gained or lost, and the work done by or on the system.

$\Delta U = q + w$

When q is negative, heat is lost by the system. When q is positive, heat is gained by the system. When w is negative, the system is doing work on the surroundings, when w is positive; work is done on the system.

The work done by or on the system is given by:

$w = -PDV$

Problem:

How much work is done when one liter of gas expands to two liters against a pressure of one atmosphere.

$w = -P\Delta V$ Si units

Note: you must use MKS units when calculating PDV so that energy units will be in Joules. Pressure is in Pascals (Pa), and has units of Newtons/$m^2$ or (kg×$m^2$/$s^2$)/$m^2$.

$w = -1.00$ atm x $1.013 \times 10^5$ Pa/atm(2 L - 1 L)x $1m^3$/1000 L $= -1.01325 \times 10^2 J$

Note: $1Pa = 1N/m^2$

Problem:

Calculate $\Delta U$ for a 1.00 L sample of gas that absorbs 100 J of heat and is expanded to 1.50 L at a constant pressure of 1.00 atm.

$\Delta U = q + w = q - PDV = 100J - 1.00$ atm x $1.013 \times 10^5$Pa/atm(.00150 $m^3$-.00100 $m^3$)

**Developing the concept of Enthalpy**

Substituting -PDV into our equation for $\Delta U$ we get

$\Delta U = q + w = q - PDV$

We can see that at constant volume that

$q_v = DU$

At constant pressure,

$q_p = DE + PDV = DH$

The quantity $q_p$ is known as the enthalpy, **$\Delta H$. It is the energy change of a system at constant pressure.** Since the changes in volume in most reactions are small, $\Delta U$ is very close to $\Delta H$.

Enthalpy is also a state function and, like $\Delta U$, can be written as:

$\Delta H = H_{products} - H_{reactants}$

<u>**Enthalpy of Reaction**</u>

Enthalpy can be thought of as heat content of the molecules. Enthalpy is an extensive property, which means it is dependent on the amount of substance present. The more of a substance you have, the greater the enthalpy. I.e. 1 pound of dynamite or 2 pounds of dynamite.

****Enthalpy change for a reaction is equal in magnitude to the enthalpy for the reverse reaction, but opposite in sign.**

****Enthalpy change for a reaction depends on the state of the reactants and the products.**

In practice the enthalpy of reaction can be calculated using the $DH_f^\circ$ which is tabulated in Appendix C by using the equation:

$\Delta H^\circ = \Sigma \Delta DH_f^\circ{}_{(products)} - \Sigma Sum\ \Delta H_f^\circ{}_{(reactants)}$

where m and n are coefficients in the balanced chemical equation.

$\Delta H_f$ = amount of heat when you form substance from its elements in their standard states.

$\Delta H_{rxn} = [\Delta H_f CO_2 + 2\Delta H_f O_2] - [\Delta H_f CH_4 + 2\Delta H_f O_2]$

$\Delta H_{rxn} = [-393.5 kJ - 2(241.6 kJ)] - [-74.9 + 0]$

Problem:

Calculate the $DH^\circ$ for the reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O_{(g)}$

## Spontaneous Processes and Entropy: The Second Law of Thermodynamics

Most processes have a natural tendency to move in one direction. We first consider the case of two bottles connected at the mouths by a stopcock, the bottle on the left is filled with a gas and the bottle o the right is evacuated. If the stopcock is opened, the gas rushes from the filled to the evacuated bottle. Why?? What about the reverse process?? It is hard to imagine all the gas staying in the filled bottle when the stopcock is opened.
This leads to a partial statement of the second law of thermodynamics.

**A Process that is spontaneous in one direction is not spontaneous in the reverse direction.**

The directional driving force for all systems is a lowering of the total energy of the system. However, how could the expansion of the gas into the evacuated chamber cause a lowering of the total energy?

**Entropy**

Entropy, S, is the measure of the randomness of a system. The more ordered a system, the lower the entropy of that system. A crystalline system has much lower entropy than a liquid system, and a liquid system has much lower entropy than a gaseous system. Particles are more ordered when their positions are confined to smaller volumes.
Spontaneous systems tend toward greater randomness; the entropy is the property that changes when the gas expands into a vacuum. This leads to the remainder of the second law:

**In any spontaneous process, there is always an increase in entropy (randomness).**

Randomness can take many forms in molecules. For instance, a triatomic gas can have several modes of vibration, rotation and translation.
The entropy change of a system is also a state function; that is it only depends upon the initial and final entropy state for the system provided that no heat enters or leaves the system; that is:

$\Delta S = S_f - S_i$

Since heat added to a system increases the entropy of a system, a more complete statement for the second law would be:

$\Delta S = S_f - S_i + q/T$

where the term q/T represents the change in entropy when heat flows into or out of the system.
It should be noted that for a spontaneous system DS > q/T and when a system is at equilibrium, DS = q/T.
Problem:
Calculate the entropy change for the following reaction under standard conditions: $CH_4 + 2O_2 \text{ ---> } CO_2 + 2H_2O_{(g)}$
Problem:
Calculate the entropy change when 10 g of ice slowly (near equilibrium) melts at 0°C.

**The second law of thermodynamics states that the total entropy of a system and its surroundings always increases for a spontaneous process.**

Since q=DH at constant pressure and temperature we can say:
DS > q/T = DH/T
which rearranges to:
DH - TDS < 0
which implies that any reaction will be spontaneous if TDS is larger than DH?

**Standard Entropies and the Third Law of Thermodynamics**

**The third law states that a perfect crystalline substance at 0K has an entropy of zero.**

As the temperature is increased by adding heat, the entropy of the system must increase as q/T. If we start at 0 K and increase the temperature to 298 K, the sum of all entropy changes (all phase changes and temperature changes) is called the standard entropy, S°. Using standard entropies, one can quantitatively calculate changes in standard entropy for a system using:

$DS = SS°_{(Products)} - SS°_{(Reactants)}$

However many times it is possible to determine the sign of DS° by just looking at the reaction and determining if the system has become more random, i.e., did the reaction form a larger number of smaller molecules, increase the moles of gas present, or was there a phase change where a solid melted or a liquid vaporize?
Problem:
What is the sign of DS° for the following reactions.
$H_2 + O_2 \text{ ---> } H_2O_{(g)}$
$H_2O_{(g)} \text{ ---> } H_2O_{(l)}$
$2NaHCO_3 \text{ ---> } Na_2CO_3 + CO_2 + H_2O$

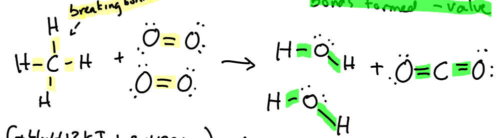
**Free-Energy**

Free energy is the energy that drives a chemical

= -802.2 kJ

breaking bond +value

bonds formed -value



(+4×413kJ + 2×498kJ) - (4×467kJ + 2×799kJ)
= -818 kJ

| ΔG== | ΔH-T | ΔS | Desc |
|---|---|---|---|
| Always + | + | - | Always nonspontaneous |
| Always - | - | + | Always spontaneous |
| | + | + | Spon. At high temp |
| | - | - | Spon. at low temp |

reaction. Recall the term:

$\Delta H - T\Delta S < 0$ implies a reaction is spontaneous. Well the $\Delta H - T\Delta S$ is defined as the free energy for the system and can have any sign. That is:

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

and **when $\Delta G$ is negative, the reaction is spontaneous.**

**When $\Delta G$ is positive, the reaction is non-spontaneous.**

**When $\Delta G$ is zero, the reaction is at equilibrium.**

As with the other thermodynamic quantities DG° values are tabulated and the standard free energy for a system can be calculated from the information in these tables.

$\Delta G^\circ = S\Delta G^\circ_{(Products)} - S\Delta G^\circ_{(Reactants)}$

Problem:

At what temperature will the production of ammonia become spontaneous assuming $\Delta S^\circ$ and $\Delta H^\circ$ are constant?

The reason $\Delta G^\circ$ is so important, is that we can use it to calculate equilibrium constants for reactions using the equation:

$\Delta G = -RT \ln K$ or $\Delta G^\circ = -2.303RT \log K$

$3H_2 + N_2 \rightarrow 2NH_3$

$\Delta H^\circ = 2\Delta H_{f\,NH_3} - 3\Delta H^\circ_{f\,H_2} - \Delta H^\circ_{f\,N_2}$

$\Delta H^\circ = 2 \times -45.9 - 0$

$= -91.8\ kJ/_{2mol}\ NH_3$

$\Delta S^\circ = 2S^\circ_{NH_3} - 3S^\circ_{H_2} - S^\circ_{N_2}$

$= 2 \times 193 - 3 \times 130.6 - 191.5$

$= -197.3\ J/_{2mol}$

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

$= -91.8 - 298(-.197)$

$\Delta G^\circ = -33.09$ <- not same -> $\Delta G^\circ = 53.4\ kJ/_{mol}$

$\Delta G^\circ = 2\Delta G^\circ_{f\,NH_3} - 3\Delta G^\circ_{f\,H_2} + \Delta G^\circ_{f\,N_2}$

$= 2 \times 26.7 - 3 \times 0 - 0$

extra credit why not same?

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

$0 = \Delta H^\circ - T\Delta S^\circ$

$\Delta H^\circ = T\Delta S^\circ$

$T = \dfrac{\Delta H^\circ}{\Delta S^\circ} = \dfrac{-91.8 kJ/2mol}{-.1973 kJ/2mol} = 465\ K$

Problem:

At 100° above the temperature calculated above for the formation of ammonia, calculate the equilibrium constant. Do the same for 100° below that temperature.

@565K

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

$= -91.8 - 565K \times (-.197) = 19.67$

$K_{eq} = e^{-\Delta G/RT}$

$= e^{-19670/8.314 \times 565}$

$= 0.015$

Since free energy is dependent upon the temperature of a system, $\Delta S$ and $\Delta H$, it is important to understand the relation between the signs of these terms.

| H° | ΔS° | ΔG° | Description |
|---|---|---|---|
| - | + | - | Always spontaneous |
| + | - | + | Always nonspontaneous |
| - | - | + or - | Spontaneous at low T nonspontaneous at high T |
| + | + | + or - | Nonspontaneous at low T spontaneous at high T |

Problem:

Why is the reaction $2HgO \rightarrow 2Hg + O_2$ possible using a Bunsen burner while $SO_2 \rightarrow S + O_2$ is not? Hint: At what temperature will HgO and $SO_2$ decompose?

Extra credit



as temp goes up & down does it become more or less spontaneous