

- Chapter 19
Chemical Thermodynamics
- Enthalpy
- A thermodynamic quantity that equal to the internal energy of a system plus the product of its volume and pressure exerted on it by its surroundings;

"Enthalpy is the amount of energy in a system capable of doing mechanical work"

Using the symbol **H** for the enthalpy:

$$H = E + p V$$

- in **endothermic** chemical reactions, the change in enthalpy is the amount of energy absorbed by the reaction;
- in **exothermic** reactions, it is the amount given off
- First Law of Thermodynamics
- You will recall from Chapter 5 that energy cannot be created nor destroyed.
- Therefore, the total energy of the universe is a constant.
- Energy can, however, be converted from one form to another or transferred from a system to the surroundings or vice versa.
- Spontaneous Processes
- Spontaneous processes are those that can proceed without any outside intervention.
- The gas in vessel *B* will spontaneously effuse into vessel *A*, but once the gas is in both vessels, it will *not* spontaneously

separate back

- Why do physical or chemical changes favor one reaction over the other
- Thermodynamics helps us to understand the directionalities of these reactions.
- Spontaneous Processes

A spontaneous process is one that proceeds on its own without any outside assistance.

Processes that are spontaneous in one direction are nonspontaneous in the reverse direction.

- Spontaneous Processes

- Processes that are spontaneous at one temperature may be nonspontaneous at other temperatures.
- Above 0°C it is spontaneous for ice to melt.
- Below 0°C the reverse process is spontaneous.
- At 0° the reactions are in equilibrium
- A spontaneous reaction can be slow like rusting of the nail or fast as an acid base reaction.
- Thermodynamics can tell us the direction and extent of the reaction but not the speed.
- What makes a process spontaneous?
- Is it true that all spontaneous processes would be exothermic.
- What makes a process spontaneous?

Is it true that all spontaneous processes would be exothermic?

- Melting, an endothermic process is spontaneous.
- Spontaneous solution processes are endothermic.
- The direction of a spontaneous change
- Apparent driving force of a spontaneous change is the tendency of the energy and matter to become disordered.
- These examples tell us that though most spontaneous processes are exothermic, there are many endothermic processes that are spontaneous.
- So there are other factors that are at work that make a process spontaneous.

Reversible and Irreversible processes.

- 1824 Sadi Carnot publishes the analysis on the factors that determine the efficiency of the steam engines.
- He stated that it is impossible to convert the energy content of the fuel completely to work because a significant amount of heat is always lost to the surroundings.
- Rudolph Clausius extended the observation and concluded that a special relationship can be derived between the ratio of the *heat delivered to an ideal engine and the temperature at which it is delivered*

$$q/T$$

He names this ratio as entropy.

- Reversible Processes

In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

- Reversible Processes

Reversible processes are those that reverse direction whenever an infinitesimal change is made in some property of the system

- Irreversible Processes
- Irreversible processes cannot be undone by exactly reversing the change to the system.
- Spontaneous processes are irreversible.

Spontaneous processes are irreversible.

Even if the system is returned to the original condition the surrounding would have changed.

- Entropy
- Entropy can be thought of as a measure of the randomness of a system.
- It is related to the various modes of motion in molecules.
- Let us see how we can relate the entropy changes to heat transfer and temperature.
- Entropy
- Like total energy, E , and enthalpy, H , entropy, S is a state function.
- Therefore,

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

- Entropy
- For a process occurring at constant temperature (an isothermal process), the change in entropy is equal to the heat that would be transferred if the process were reversible divided by the temperature:

at constant temperature

(Rudolph Clausius)

- Since S is a state function, we can use this equation to calculate the ΔS for any process.
- ΔS For Phase Change

Consider the melting of ice

- At 1 atm and 0°C ice and water are in equilibrium with each other.
- If we melt one mole of ice at $0^\circ\text{C}/1$ atm to form 1 mole of water still at 0°C
- We need to give the water heat that would be equal to ΔH_{fusion} .
- If the process is done extremely slowly the process can be reversible if we remove that amount of heat.
- Dictionary Meaning for Entropy

A measure of the unavailable energy in a closed thermodynamic system

that is also usually considered to be a measure of the system's disorder,

that is a property of the system's state, and

that varies directly with any reversible change in heat in the system and inversely with the temperature of the system;

broadly : the degree of disorder or uncertainty in a system

- Calculating change in entropy
- Transferring 100kJ of heat to a large mass of water at 0°C results in a change in entropy of
- Same transfer at 100°C results in
- Increase in entropy is greater at lower temperature

Example 9.2

The element mercury, Hg, is a silvery liquid at room temperature. The normal freezing point of mercury is -38.9°C , and its molar enthalpy of fusion is $\Delta H_{\text{fusion}} = 2.29$ kJ/mol.

What is the entropy change of the system when 50.0 g of Hg(*l*) freezes at the normal freezing point?

1. Convert the g of Hg to moles

2. The enthalpy of fusion calculate the heat that would be exchanges for this amount in joules. Remember that freezing is an exothermic process so the energy is going to leave the system so it will have a negative value

$$-\Delta H_{\text{fusion}} = -2.29 \text{ kJ/mol}$$

3. Convert the temperature to K

4. Now plug this in the formula

5. This would be a negative value because heat flows from the system.

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The normal boiling point of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is 78.3°C , and its molar enthalpy of vaporization is 38.56 kJ/mol. What is the change in entropy in the system when 68.3 g of $\text{C}_2\text{H}_5\text{OH}(g)$ at 1 atm condenses to liquid at the normal boiling point?

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Answer: -163 J / K

- There are many versions of the second law, but they all have the same effect, which is to explain the phenomenon of irreversibility in nature

- Second Law of Thermodynamics

The entropy of an isolated system tends to increase.

- Second Law of Thermodynamics
- Entropy increases in any spontaneous

(irreversible) process whereas a non spontaneous (reversible) process results in no overall change in entropy.

- The sum of the entropy change of the system and surroundings for any spontaneous process is always greater than zero
- What happens when a mole of ice melts in our hand
- Example of melting ice in the hand.
- The entropy change we calculated earlier for melting of ice:
- The surrounding here is the hand and the body temperature is

$$37^{\circ}\text{C} = 310\text{K}$$

- Thus the total entropy change is positive
- If the temperature of the surrounding (in this case the hand,) was infinitesimally close to 273K the entropy change would have been zero and

then the reaction would have been reversible

- Second Law of Thermodynamics

In other words:

For reversible processes:

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

For irreversible processes:

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

- Second Law of Thermodynamics

The second law of thermodynamics states that the entropy of the universe increases for spontaneous processes, and the entropy of the universe does not change for reversible processes.

- Second Law of Thermodynamics

These last truths mean that as a result of all spontaneous processes the entropy of the universe increases.

- Entropy on the Molecular Scale
- Ludwig Boltzmann described the concept of entropy on the molecular level.
- Temperature is a measure of the average kinetic energy of the molecules in a sample.
- Entropy on the Molecular Scale
- Molecules exhibit several types of motion:
 - Translational: Movement of the entire molecule from one place to another.
 - Vibrational: Periodic motion of atoms within a molecule.
 - Rotational: Rotation of the molecule on about an axis or rotation about σ bonds.
- Entropy on the Molecular Scale
- Boltzmann envisioned the motions of a sample of molecules at a particular instant in time.
 - This would be similar to taking a snapshot of all the molecules.
- He referred to this sampling as a microstate of the thermodynamic system.
- Entropy on the Molecular Scale
- Each thermodynamic state has a specific number of microstates, W , associated with it.
- Entropy is

$$S \propto \ln W$$

$$S = k \ln W$$

where k is the Boltzmann constant, 1.38×10^{-23} J/K.

- Entropy on the Molecular Scale
- The change in entropy for a process, then, is

$$\Delta S = k \ln W_{\text{final}} - k \ln W_{\text{initial}}$$

- Entropy on the Molecular Scale

- The number of microstates and, therefore, the entropy tends to increase with increases in
 - Temperature.
 - Volume.
 - The number of independently moving molecules.
- Entropy and Physical States
- Entropy increases with the freedom of motion of molecules.
- Therefore,

$$S(g) > S(l) > S(s)$$
- Solutions

Generally, when a solid is dissolved in a solvent, entropy increases.
- Entropy Changes
- In general, entropy increases when
 - Gases are formed from liquids and solids.
 - Liquids or solutions are formed from solids.
 - The number of gas molecules increases.

(c) The HCl sample has the higher entropy because the HCl molecule is capable of storing energy in more ways than is Ar. HCl molecules can rotate and vibrate; Ar atoms cannot.

Choose the sample of matter that has greater entropy in each pair, and explain your choice: **(a)** 1 mol of NaCl(s) or 1 mol of HCl(g) at 25°C, **(b)** 2 mol of HCl(g) or 1 mol of HCl(g) at 25°C, **(c)** 1 mol of HCl(g) or 1 mol of Ar(g) at 298 K.

- Third Law of Thermodynamics

The entropy of a pure crystalline substance at absolute zero(0 K)

is 0.

$$S = k \ln W$$

At 0 K there is no thermal motion and so there is only one microstate

Therefore

- When we see this now the Kelvin scale makes more sense an absolute zero seems like the more scientific place to start.
- As the temperature increases the atoms and molecules in the crystal gain energy in the form of vibrational motion about their lattice positions.
- Then the microstates and hence the entropy of the system increases.
- The entropy of phases of given substance follows the order

$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$

- At phase Changes
- At the melting points there is a sharp increase in the entropy as the phase of the matter changes and the molecules have more freedom to move about in the entire volume of the substance.
- At the boiling point an abrupt change in entropy occurs as the molecules get a lot of space to move about.
- Standard Entropies

These are molar entropy values of substances in their standard states.

Why 298 K?

298.15 is the conventional temperature for reporting data.

Standard state of any substance is defined as the pure substance at 1 atm pressure

The substance will be solid liquid or gas depending on its nature.

Standard entropies are denoted as S° .

Standard molar entropies of gases is higher than solids.

Standard entropies tend to increase with increasing molar mass between elements.

Standard molar entropies increases with the increase in the number of atoms in a molecule

- About Graphite and Diamond

Standard molar entropies

Graphite 5.7 J / K mol

Diamond 2.4 J / K mol

The C atoms in Diamond are more rigid than Graphite.

- Standard Entropies

Larger and more complex molecules have greater entropies.

- Entropy Changes in Chemical Reactions

Entropy changes for a reaction can be estimated in a manner analogous to that by which ΔH is estimated:

$$\Delta S^\circ = \sum n \Delta S^\circ (\text{products}) - \sum m \Delta S^\circ (\text{reactants})$$

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

- **SAMPLE EXERCISE 19.5**

Answer: 180.39 J/K

- The section on entropy change in the surrounding (page 818):
- Read carefully and explain in detail with equations why synthesis of ammonia is a spontaneous process at 298 K.
- Please do not just copy down the section. Write in your own words.
- Entropy Changes in Surroundings
- Heat that flows into or out of the system changes the entropy of the surroundings.
- For an isothermal process:
- Gibbs Free Energy
- Though we have learnt in this chapter that the spontaneous process is one in which there is an increase in the entropy of a system we do come across some spontaneous processes that result in a decrease in the entropy of the system!
- An example is the highly exothermic process of reaction of sodium metal with chlorine gas to form sodium chloride.
- Spontaneous processes that result in a decrease in entropy are always exothermic.
- So this suggests that enthalpy also has something to do with spontaneity.
- Gibbs Free Energy

- Willard Gibbs proposed a new state function *now* named Gibbs Free Energy (G):

$$G = H - TS$$

Enthalpy term Entropy term

Where T is the absolute temperature.

Change in free energy of the system

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

Under standard conditions this becomes

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

- Entropy Change in the Universe
- The universe is composed of the system and the surroundings.
- Therefore,

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

Since

- This becomes:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} +$$

Multiplying both sides by $-T$,

$$-T\Delta S_{\text{universe}} = -T\Delta S_{\text{system}} + \Delta H_{\text{system}}$$

$$-T\Delta S_{\text{universe}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}}$$

We know from before

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

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

- $-T\Delta S_{\text{universe}}$ is defined as the Gibbs free energy, ΔG .

- It is more convenient to use ΔG as the criterion for spontaneity than $\Delta S_{\text{universe}}$ because ΔG relates to the system and avoids the complication of having to study the surroundings

When $\Delta S_{\text{universe}}$ is positive, ΔG is negative.

Therefore, when ΔG is negative, a process is spontaneous.

- Gibbs Free Energy

We know that the $\Delta S_{\text{universe}}$ for a spontaneous process is always positive

1. If ΔG is negative, the forward reaction is spontaneous.
2. If ΔG is 0, the system is at equilibrium.
3. If ΔG is positive, the reaction is spontaneous in the reverse direction.

At constant P and T

In any spontaneous process at constant pressure and temperature the free energy of the system always decreases

- Let us remember Reaction Quotient Q
- If $Q = K$,
- Standard Free Energy Changes

Analogous to standard enthalpies of formation ΔH° , are standard free energies of formation, ΔG° .

The fact that ΔG° is negative tells us that the reaction would proceed spontaneously in the forward direction to form more PCl_3 .

(b) What is ΔG° for the reverse of the above reaction?

- $\text{CH}_4(\text{g})$ -50.8 kJ/mol
- $\text{CO}_2(\text{g})$ -394.4
- $\text{H}_2\text{O}(\text{g})$ -228.57

- $\text{CH}_4(\text{g})$ -50.8 kJ/mol
- $\text{CO}_2(\text{g})$ -394.4
- $\text{H}_2\text{O}(\text{g})$ -228.57

Answer: -800.7 kJ

- (a) Without using data from Appendix C, predict whether ΔG° for this reaction is more negative or less negative than ΔH° .

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

- (a) We see that the reactants consist of six molecules of gas, and the products consist of three molecules of gas and four molecules of liquid.

Thus, the number of molecules of gas has decreased significantly during the reaction.

we would expect a number of gas molecules to lead to a decrease in the entropy of the system—the products have fewer accessible microstates than the reactants.

We therefore expect ΔS° and $(T \Delta S^\circ)$ to be negative numbers.

Because we are subtracting $T \Delta S^\circ$, which is a negative number, we would predict that ΔG° is less negative than ΔH° .

- (b) Use data from Appendix C to calculate the standard free-energy change for the reaction at 298 K. Is your prediction from part (a) correct?

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

Answer: lower

- Free Energy Changes

At temperatures other than 25° C,

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

How does ΔG° change with temperature?

- Free Energy Changes

At temperatures other than 25° C,

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

How does ΔG° change with temperature?

- Free Energy and Temperature
- There are two parts to the free energy equation:
 - ΔH° — the enthalpy term
 - $T\Delta S^\circ$ — the entropy term
- The temperature dependence of free energy, then comes from the entropy term.
- Free Energy and Temperature
- Generally ΔH and ΔS do not change much with temperature, but the magnitude of $T\Delta S$ changes directly with temperature.

Under standard conditions:

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

The values of ΔH° and ΔS° can be obtained from any source and they change very little with temperature, the value of ΔG° can be calculated.

Assume that ΔH° and ΔS° for this reaction do not change with temperature.

(a) Predict the direction in which ΔG° for this reaction changes with increasing temperature.

We expect this reaction to have a negative ΔS as the number of molecules is decreasing

So $-T\Delta S^\circ$ will be positive and will increase with the increase in temperature.

So G keeps becoming larger with increase in temperature and the reaction becomes less inclined to go forward.

•

(b) Calculate the values of ΔG° for the reaction at 25°C and 500°C .

Now:

ΔH will be calculated as we learnt in chapter 15 and ΔS in this chapter

Then plug the values in the above equation

- Homework Question

Practice Exercise on page 829.

I want to see all the work done **fully**. I want to see the formula written, plugged and then the answer.

NO SHORTCUTS

Again I will collect it **either in the first five or the last five minutes of class**.

- So far we learnt to calculate the value of ΔG under standard conditions.
- Now we will learn to calculate the ΔG under non standard conditions.

And

- We will learn to relate the value of ΔG° with the equilibrium constant K .
- Free Energy and Equilibrium

The relationship between the standard free energy change and the nonstandard free energy change is

$$\Delta G = \Delta G^\circ + RT \ln Q$$

\

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Under standard conditions, all concentrations are 1 M ,

so $Q = 1$ and

the $\ln Q = 0$

the last term drops out.

$$\Delta G = \Delta G^\circ$$

- We know that phase change, say boiling point, is an equilibrium condition and at equilibrium $\Delta G = 0$
- So ΔG° becomes 0
- Free Energy and Equilibrium
- At equilibrium, $Q = K$, and $\Delta G = 0$.
- The equation becomes

$$0 = \Delta G^\circ + RT \ln K$$

- Rearranging, this becomes

$$\Delta G^\circ = -RT \ln K$$

or,

$$K = e^{-\Delta G^\circ/RT}$$

SAMPLE EXERCISE 19.9 Relating ΔG to a Phase Change at Equilibrium

As we saw in Section 11.5, the *normal boiling point* is the temperature at which a pure liquid is in equilibrium with its vapor at a pressure of 1 atm. **(a)** Write the chemical equation that defines the normal boiling point of liquid carbon tetrachloride, $\text{CCl}_4(l)$. **(b)** What is the value of ΔG° for the equilibrium in part (a)? **(c)** Use thermodynamic data in Appendix C and Equation 19.20 to estimate the normal boiling point of CCl_4 .

-
- The formula we need to use is :
- We need Q for this so

$$K = e^{-\Delta G^\circ/RT}$$

- Homework Question
- Chapter 17

Question # 30

I will check for correctness.

Look at all the fun you have been missing!!!!

- QUESTION#19.73

The reaction is $2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$

$$\Delta G = \Delta G^\circ + RT \ln K$$

- $\Delta G = \Delta G^\circ + RT \ln$

Question #17.29

- You have to prepare a pH 3.5 solution and you have 0.1 M HCHO_2 and 0.1 N NaCHO_2 . How many ml of each solution would you use.

$$K_a = 1.8 \times 10^{-4}$$

- Homework question
- 19.29
- Show all work to get credit.