Entropy and the 2nd and 3rd Laws of Thermodynamics

Overview

The **entropy** of an object is a measure of the amount of energy which is unavailable to do work. **Entropy** is also a measure of the number of possible arrangements the atoms in a system can have. In this sense, **entropy** is a measure of uncertainty or randomness.

Chemical thermodynamics (thermochemistry) is the study of energy flow during a chemical reaction.

Thermodynamics allows you to:

1. predict whether or not a reaction will occur (equivalent to comparing Q to K)
2. calculate K_{eq} from ΔH^o and ΔS^o and Temperature (In expt. 12H part C, you will do the opposite. You will determine ΔH^o and ΔS^o by measuring how K_{eq} changes with temperature.)
3. understand why some reactions have large K's while others have small K's

Thermodynamics was developed long before atoms and molecules were discovered. **Historically, thermodynamics was developed by people with a very practical goal: To maximize the efficiency of a steam engine! That is, they wanted to know the most efficient way of converting heat into work.**

There are seven important thermodynamic parameters (state functions). You are already familiar with six of these:

P (pressure), V (volume), T (temperature), H (enthalpy), S (entropy), and E (internal energy)

Enthalpy is a concept used in science and engineering when heat and work need to be calculated. ... When a substance changes at constant pressure, **enthalpy** tells how much heat and work was added or removed from the substance. **Enthalpy** is similar to energy, but not the same.
Enthalpy change is the name given to the amount of heat evolved or absorbed in a reaction carried out at constant pressure. It is given the symbol ΔH, read as "delta H".

Review of The First Law of Thermodynamics

The change in the value of a **state function** during a reaction depends only on the initial and final states of the reactants and products **not** on the path between them.

First law of thermodynamics (conservation of energy): The energy of the universe (system + surroundings) is constant. Energy is never created or destroyed in a chemical reaction; it is merely transferred between the system (reaction) and surroundings in the form of heat or work.

$\Delta E_{system} = q + w$ (mathematical expression of the first law)

Where q is heat absorbed by the system **from the surroundings**; w is work done on the system **by the surroundings**. We will assume that the only way a reaction can do work **on the surroundings** (negative work) is through the expansion of gases (called "P-V" work). Thus, at constant pressure:

w = -PΔV

Positive work (work done on the system) corresponds to a **decrease** in volume (negative ΔV).

q and w are **NOT** state functions. For example, the heat absorbed by the system depends on whether the process is done at constant volume or constant pressure because the amount of work done on the system differs:

At constant volume, w = 0 so:
ΔE = q$_v$

At constant pressure, w = -PΔV so:
ΔE = q$_p$ - PΔV
ΔE + PΔV = q$_p$
ΔH = q$_p$ **(Enthalpy is defined as: H = E + PV)**

ΔE = ΔH - PΔV

If volume changes are small then ΔE is not much different than ΔH

Standard enthalpy change (ΔH°) is the enthalpy change when reactants in their standard state are converted to products in their standard state. "Standard" states are simply convenient reference states that allow thermodynamic quantities (state functions) to be tabulated and compared (see appendix 3). The standard states are as follows:

State of matter	Standard state
Solid	**Pure solid at 1 atm**
Liquid	**Pure liquid at 1 atm**
Gas	**1 atm partial pressure**
Solution	**1 M concentration**

Temperature is NOT specified but thermodynamic data is usually tabulated for 298 K (25°C)

TABLE 15–1 Simple Thermodynamic Processes and the First Law		
Process	**What is constant:**	**The first law, $\Delta U = Q - W$, predicts:**
Isothermal	$T = $ constant	$\Delta T = 0$ makes $\Delta U = 0$, so $Q = W$
Isobaric	$P = $ constant	$Q = \Delta U + W = \Delta U + P\,\Delta V$
Isovolumetric	$V = $ constant	$\Delta V = 0$ makes $W = 0$, so $Q = \Delta U$
Adiabatic	$Q = 0$	$\Delta U = -W$

Spontaneous processes and the directionality of chemical reactions

A "spontaneous process" is one that occurs **without** the **continuous** input of energy. (Even spontaneous processes need at least a small input of energy to get them started. This is the activation energy.)

What determines whether a reaction will occur spontaneously? In general, **any reaction or process that is not at equilibrium will proceed spontaneously toward equilibrium.**

We will see that we can use thermodynamic data (measurement of heat flow) to determine whether a reaction is at equilibrium. The "driving force" for a reaction is the "tendency" for a system to achieve **minimum energy** and **maximum entropy**.

> If $\Delta H < 0$ and $\Delta S > 0$ then the reaction has a very large K_{eq}. **The forward reaction is spontaneous except when Q is very large.** Such reactions go to completion.

> If $\Delta H > 0$ and $\Delta S < 0$ then K_{eq} is very small. **The reverse reaction is spontaneous except when Q is very small.** The reverse reaction goes to completion.

> If ΔH and ΔS have the same sign, then the size of K_{eq} and the direction in which the reaction proceeds depends on the relative sizes of ΔH and ΔS (and on temperature) and the value of Q. (The magnitudes of ΔH and ΔS depend on the value of Q.) This type of reaction usually has a finite equilibrium constant and reaches equilibrium.

The Second Law of Thermodynamics: The Criterion for Spontaneity

The second law of thermodynamics says that the entropy of any isolated system always increases. Isolated systems spontaneously evolve towards thermal equilibrium—the state of maximum entropy of the system. More simply put: the entropy of the universe (the ultimate isolated system) only increases and never decreases.

A simple way to think of the second law of thermodynamics is that a room, if not cleaned and tidied, will invariably become more messy and disorderly with time – regardless of how careful one is to keep it clean. When the room is cleaned, its entropy decreases, but the effort to clean it has resulted in an increase in entropy outside the room that exceeds the entropy lost.

The first law of thermodynamics (conservation of energy) does not forbid the strange events described above but the second law does!

To understand the second law of thermodynamics we need to understand the concept of entropy in terms of disorder or the number of **"microstates"** available to a system. A system has more entropy if its energy content is "spread out" among more microstates.

In keeping with our everyday experience, the second law says that whenever something happens, the **universe (system + surroundings)** gets messier (entropy increases). If this was **not** true then it would

be possible to generate spontaneous order and for heat to flow from cold to hot! **(see optional material for the proof).**

If you watch a movie, how can you tell if it is running backwards? Entropy is sometimes referred to as the "arrow of time".

1. State the second law in words.

The entropy of the universe increases whenever a spontaneous process occurs. Entropy is <u>not</u> conserved.

The entropy of the universe does not change when an equilibrium process occurs.

2. Give the mathematical statement of the second law.

For a spontaneous process: $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$ **or** $\Delta S_{surroundings} > -\Delta S_{system}$
For an equilibrium process: $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$ **or** $\Delta S_{surroundings} = -\Delta S_{system}$

<u>**The Third Law of Thermodynamics: Absolute entropy**</u>

Ludwig Boltzmann showed that the entropy of a system is related the number of microstates (W) available to the system.

$S = k \ln W$ where k is called "Boltzmann's constant".   **k = 1.38 x 10^{-23} J/K.**

1. If there is only one microstate available to a system, then S = **0.**

2. What kind of system would have only one microstate available? (This is the 3rd law!)

A system with perfect order: a perfect crystal at absolute zero (-273ºC = 0 K). A perfect crystal has no defects (gaps, misaligned molecules, etc.) At absolute zero, there is no molecular motion so every molecule is in a perfectly well-defined position.

Notice that the unit for entropy is the same as the unit for heat capacity (J/K or J/ºC). The entropy for a mole of a substance is expressed as J/mol-K or J/mol-ºC (a molar heat capacity!). The reason for these units is explained below.

Like enthalpy, entropy is a state function. However, unlike enthalpy (for which only *changes*, ΔH, can be measured), it is possible to measure the *absolute entropy* (S) of a given amount of a substance at a specified temperature and pressure. This is possible because one can assign a "zero point" of entropy (perfect order). The graph below shows how the **absolute** entropy varies with the temperature and physical state of a pure substance.
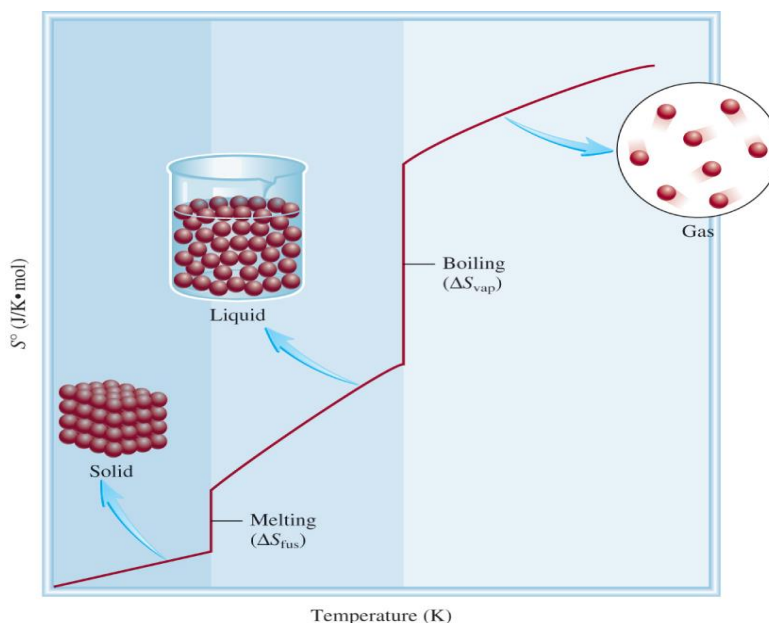
The absolute entropy of a pure substance clearly depends on the temperature. The entropy of a substance at a given temperature is determined by measuring the heat capacity of the substance as a function of temperature.

Calculating ΔS^o of the system

Absolute <u>molar</u> entropies at 25ºC for pure substances in their standard states (S^o) are listed in Handbooks. (Molar entropy is the amount of entropy contained in 1 mole of a substance.) These numbers allow us to calculate the standard entropy change (ΔS^o) for any reaction! Since entropy is a state functions, one can calculate ΔS^o as follows:

$\Delta S^o =$ total entropy of the products – total entropy of the reactants
$\Delta S^o = \Sigma \, nS^o$ (products) - $\Sigma \, mS^o$ (reactants)

3. Predict the sign for ΔS^o and then calculate ΔS^o and ΔH^o from the data in Handbooks.

a) $CO(g) + 2H_2(g) = CH_3OH(l)$ Predicted Sign for ΔS^o? ___**negative**_____

$\Delta S^o = 126.8$ J/mol-K $– 197.9$ J/mol-K $– 2(131.0$ J/mol-K$) = -333.1$ J/mol-K (unfavorable)

Negative as predicted!

$\Delta H^o = -238.7$ kJ/mol $– (-110.5$ kJ/mol$) – 0$ kJ/mol $= -128.2$ kJ/mol (favorable)

The reaction produces one molecule from 3 molecules. The reactants are gases and the product is a liquid. Both of these predict a negative change in entropy. The reaction produces order. This is an

unfavorable situation and tends to make the equilibrium constant small. However, the reaction is also exothermic, which tends to make the equilibrium constant large. The actual magnitude of K_{eq} depends on the relative magnitudes of ΔH and ΔS and on the temperature.

b) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ Predicted Sign for ΔS^o? ____**Positive**_____

ΔS^o = 39.8 J/mol-K + 213.6 J/mol-K – 92.9 J/mol-K) = 160.5 J/mol-K (favorable)

Positive as predicted!

ΔH^o = -635.6 kJ/mol + (-393.5 kJ/mol) – (-1206.9 kJ/mol) = 178.0 kJ/mol (unfavorable)

The reaction produces two molecules from 1 molecule. The reactant is a solid and one of the products is a gas. Both of these predict that entropy will increase. The reaction produces disorder. This is a favorable situation and tends to make the equilibrium constant large. However, the reaction is also endothermic, which tends to make the equilibrium constant small. The actual magnitude of K_{eq} depends on the relative magnitudes of ΔH and ΔS and on the temperature.

For both reactions, ΔH^o and ΔS^o have the same signs. One is favorable and the other is unfavorable so both reactions will reach equilibrium.

Calculating ΔS^o of the surroundings

Entropy changes occur whenever heat is transferred between a system and its surroundings. The *magnitude* of the entropy change depends on the *temperature* at which the process occurs. For a reaction taking place at constant temperature:
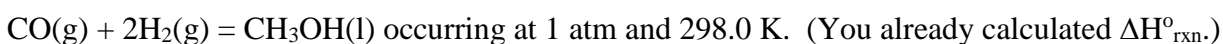
$$\Delta S^o_{surr} = \frac{-\Delta H^o_{rxn}}{T_{rxn}}$$

(Note: For technical reasons, this equation can NOT be used to calculate ΔS^o of the system. See optional material to understand why and to see where this equation comes from.)

Now you can see why the unit for S is the same as the unit for heat capacity.

Applying the 2nd Law of Thermodynamics

4. Calculate ΔS^o_{surr} for the following reaction:

$CO(g) + 2H_2(g) = CH_3OH(l)$ occurring at 1 atm and 298.0 K. (You already calculated ΔH^o_{rxn}.)

$$\Delta S^o_{surr} = \frac{128.2 \frac{kJ}{mol}}{298.0 \, K} = 0.4300 \text{ kJ/mol-K} = 4300 \text{ J/mol-K}$$

The reaction added heat to the surroundings so the entropy went up.

5. In problem 5a you calculated ΔS^o for this reaction (ΔS^o_{sys}). Copy the answer here: **-333.1 J/mol-K.** The first law of thermodynamics says the $\Delta H_{surr} = -\Delta H_{sys}$. Notice that $\Delta S_{surr} \neq -\Delta S_{sys}$ for this reaction (entropy is NOT conserved!) Why?

$\Delta S_{surr} > -\Delta S_{sys}$ so the reaction is <u>not</u> at equilibrium under standard conditions.

6. Use the second law of thermodynamics to determine whether the forward or reverse reaction is spontaneous **under standard conditions** at 298 K.

$\Delta S^o_{universe} = \Delta S^o_{system} + \Delta S^o_{surroundings}$ = -331.1 J/mol-K + 430.0 J/mol-K = 96.9 J/mol-K

The entropy of the universe increases so this reaction is spontaneous under standard conditions. The heat produced by the reaction increased the entropy of the surroundings enough to compensate for the decrease in the entropy of the system.

7. When you say that a reaction is performed under "standard conditions", you mean that, initially, all reactants AND products are present in their standard states. Thus, the initial concentration of all aqueous species is 1.00 M and the initial pressure of all gases is 1.00 atm. Under standard conditions, what is the initial value of Q?

$$Q = 1$$

8. What do your results in problem 8 tell you about the magnitude of the equilibrium constant for the reaction? (Remember what the relationship between Q and K_{eq} tells you!)

We concluded that the forward reaction was spontaneous under standard conditions when Q = 1. So we know that Q < K and, therefore, <u>K > 1</u> (at 298 K).

9. Use the second law of thermodynamics to calculate the temperature at which the reaction would be at equilibrium under standard conditions. What is the value of the equilibrium constant at this temperature?

At equilibrium: $\Delta S^o_{universe} = \Delta S^o_{system} + \Delta S^o_{surroundings} = 0$

$\Delta S^o_{surroundings} = -\Delta S^o_{system}$

$-\Delta H^o_{sys}/T = -\Delta S^o_{system}$

$T = \Delta H^o_{sys}/\Delta S^o_{sys}$

$T = (-128.2 \text{ kJ/mol}) / (-0.3331 \text{ kJ/mol-K}) = 384.9 \text{ K}$

At this temperature, the reaction is at equilibrium so Q = K. Since Q = 1 under standard conditions:

K = 1

Notice that K decreased when the temperature increased as expected for an exothermic reaction.