Entropy

CHEM 361A: Introduction to Physical Chemistry

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Lecture 7

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Learning Objective: Develop statistical mechanical concepts and use them to derive the internal energy and heat capacity.
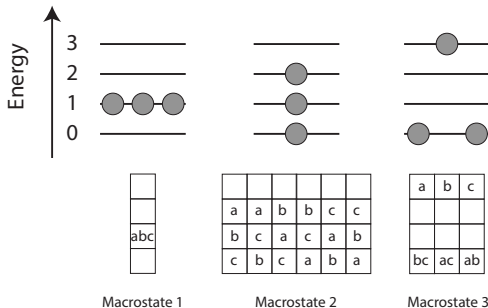
References:

- Atkins and de Paula Focus 3A - 3C
- Chang Chapter 5

Entropy

Entropy is defined as:

$$S = k_B \ln W$$

Entropy is a measure of uncertainty. This uncertainty is quantified as the number of states that a system can occupy given a total energy for the system.

In our three molecule example with $E_{tot}=3$:

- $S_{W_1} = k_B \ln 1 = 0$
- $S_{W_2} = k_B \ln 6$
- $S_{W_3} = k_B \ln 3$

Spontaneity

Enthalpy can be used to define reactions at constant pressure that are:

- **Exothermic**: Heat transferred from the system to the surroundings
- **Endothermic**: Heat transferred from the surroundings to the system

There is a tendency to use these terms to describe the how *favourable* the reaction is. However, this does not indicate if the process will happen.

- A **spontaneous** process: A process that has a tendency to occur without work needing to be done.
- A **nonspontaneous** process: A process that can only happen by doing work.

The spontaneity of a process says nothing about the rate at which it occurs.

Examples of Spontaneous Changes

- Gas expanding to fill a volume

- A plate shattering:
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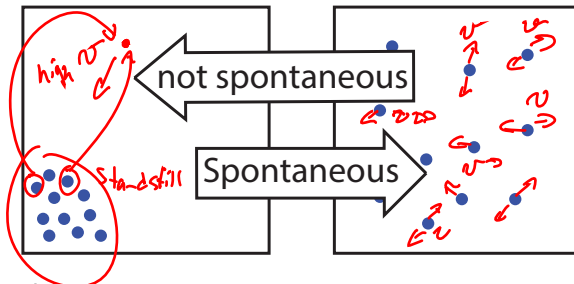
Entropy and Spontaneity

Here is what we know

- Entropy is a measure of the order of magnitude of the number of microstates in a given macrostate.
- Each microstate is equally likely, therefore the macrostates with more microstates are more probable to be observed.
- Therefore, systems will tend to move towards macrostates with higher entropy as they will naturally find these macrostates randomly

This means that spontaneity and entropy are linked since processes which increase entropy are spontaneous.

The Second Law of Thermodynamics

The **Second Law of Thermodynamics** states that:

- The entropy of an isolated system tends to increase

One way to quantify this statement as an equation is

$$\Delta S = \frac{q_{rev}}{T}$$

- q is used (instead of fx. work) because a quantity that describes chaos should be quantified with a transfer of energy that quantifies random motion
- q_{rev} means that the heat is transferred in small packets and dispersed evenly
- T in the denominator takes into account the entropy already present for a system at a specified temperature
- Entropy is also a state function

ΔS Example

Calculate ΔS for a reversible transfer of 100 kJ of heat to a large mass of water at:

1. 273 K

ΔS During the Expansion of a Gas

Recall for the isothermal ($\Delta T = 0$) expansion of an ideal gas that

$$w = -q$$

since $w = -nRT \ln \frac{V_f}{V_i}$ for an isothermal, reversible expansion, then

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

Note that even though we used a *reversible* transfer of heat to find this relationship, ΔS is a state function so this result is valid for irreversible changes.

ΔS During the Expansion of a Gas Example

Calculate the change in molar entropy when a sample of hydrogen gas expands isothermally to twice its initial volume by

1. a reversible process
2. an irreversible process

ΔS During Heating

It is expected that the entropy of a system increases with an increase in temperature. To show this we will start with

$$dS = \frac{dq_{rev}}{T}$$

since $dq = CdT$, then

$$dS = \frac{CdT}{T}$$

Integrating both sides yields

$$\Delta S = C \ln \frac{T_f}{T_i}$$

Note that if the process is at constant volume or pressure, it is alright to substitute the corresponding heat capacity term in.

ΔS During Heating Example

Calculate the change in molar entropy when a sample of hydrogen gas is heated from 20°C to 30°C at a constant volume ($C_{V,m} = 22.44$ J K^{-1} mol^{-1}).
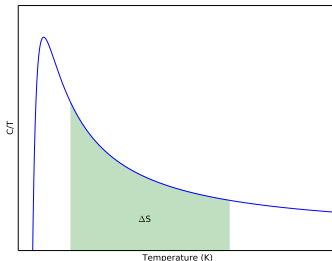
ΔS and Not Constant Heat Capacity

When the heat capacity cannot be considered a constant (fx. solids at very low temperatures) the starting point is still:

$$dS = \frac{CdT}{T}$$

A substitution for the function that describe C is inserted and integrated:

$$\Delta S = \int_{T_i}^{T_f} \frac{CdT}{T}$$

ΔS and Phase Transitions

Things to note at phase boundaries:

- The entropy of a substance increases when it melts and when it vapourises.
- The transfer of energy as heat when the substance is at its melting/boiling point is reversible
- If the pressure is held constant then

$$\Delta_{fus}S = \frac{\Delta_{fus}H(T_{fus})}{T_{fus}} \quad \text{and} \quad \Delta_{vap}S = \frac{\Delta_{vap}H(T_{vap})}{T_{vap}}$$

ΔS and Phase Transition Examples

Calculate the entropy of vapourisation of water at

1. 25°C

given that $C_{p,m}(H_2O(l))$= 75.29 J K^{-1} mol^{-1}, $C_{p,m}(H_2O$ (g))= 33.58 J K^{-1} mol^{-1}, and $\Delta_{vap}H(373$ K)= 40.7 kJ mol^{-1}

ΔS in the Surroundings

Using the same definition as before, ΔS of the surroundings in contact with the system is:

$$\Delta S_{sur} = \frac{q_{sur,rev}}{T}$$

Since the surroundings are so enormous compared to the system its pressure will not change, so

$$\Delta S_{sur} = \frac{\Delta H_{sur}}{T}$$

Since H is a state function, then it does not matter if the process is reversible or not. As a result:

$$\Delta S_{sur} = \frac{q_{sur}}{T} = -\frac{q}{T} = -\frac{\Delta H}{T}$$

ΔS in the Surroundings Examples

A perfect gas expands isothermally from V_i to V_f. Calculate the entropy change in the surroundings if

1. the gas expands reversibly.
2. freely ($p_{ex} = 0$).
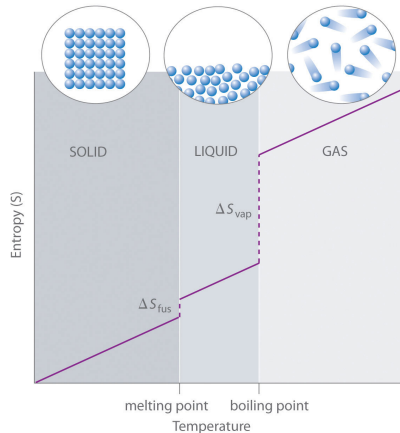
The Third Law of Thermodynamics

The Third Law of Thermodynamics states that the entropies of all perfectly crystalline substances are the same at $T = 0$.

- The convention is to set $S(T = 0) = 0$ (only one arrangement in perfectly crystalline substance):

$$S = k_B \ln W = k_B \ln 1 = 0$$

- To find the absolute entropy of a substance:

$$S = S_T - S_0 = \int_0^T \frac{C_p}{T} dT$$

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Residual Entropies

Not every substance is perfectly crystalline at $T = 0$ K.

- Vibrational modes still present
- Different orientations of molecules
  - CO (pictured below), may arrange in either direction semi-randomly.

Perfect arrangement   Imperfect arrangement

The residual entropy is the actual entropy of a substance at $T = 0$ K.

Third Law Questions

1. Estimate the residual entropy of 1 mol of CO.
2. Determine the absolute entropy of CO at 16 K.

Hint: $C_p = 9.5 \times 10^{-4} T^3$

Standard Molar Entropy

The standard molar entropy represents

$$S^{\ominus} = \int_{0K}^{298K} \frac{C_p}{T} dT \; ; \quad P = 1 \text{ bar}$$
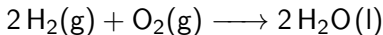
These values can be used in the same way as the $\Delta H^{\ominus}$ to find the change in entropy for a reaction:

$$\Delta_r S^{\ominus} = \sum \nu S^{\ominus}(products) - \sum \nu S^{\ominus}(reactants)$$

Finding the $\Delta_r S^{\ominus}_{Total}$ indicates if the reaction is spontaneous.

Standard Molar Entropy Example

The combustion of $H_2(g)$ at 298 K is as follows:

$$2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$$

1. Calculate $\Delta S^{\ominus}_{sys}$
   Hint:
   - $S^{\ominus}(H_2(g)) = 130.684$ J K^{-1} mol^{-1}
   - $S^{\ominus}(O_2(g)) = 205.138$ J K^{-1} mol^{-1}
   - $S^{\ominus}(H_2O(l)) = 69.91$ J K^{-1} mol^{-1}

2. Calculate $\Delta S^{\ominus}_{surr}$
   Hint: $\Delta_f H^{\ominus}(H_2O) = -285.8$ kJ mol^{-1}

3. Determine $\Delta S^{\ominus}_{total}$

Summary

- Entropy is defined as

$$S = k_B \ln W$$

- A spontaneous process is a process that has a tendency to occur without work needing to be done.

- The Second Law of Thermodynamics states that the entropy of an isolated system tends to increase

- The Third Law of Thermodynamics states that the entropies of all perfectly crystalline substances are the same at T= 0

- These two laws of thermodynamics can be used to quantify if a process is spontaneous