

Lecture #14: Entropy and the second Law of Thermodynamics

Homework #5: Chapter 20 – 8, 9, 13, 14; Chapter 21 – 2, 8, 46, 47

I. Entropy, Spontaneous Processes & 2nd Law of Thermodynamics

II. Boltzmann-Planck Equation: $S = k \ln w$

I. Entropy, Spontaneous Processes & 2nd Law of Thermodynamics

Systems will spontaneously go from nonequilibrium to equilibrium.

There are some spontaneous processes which do not lead to a lowering of energy ($\Delta U < 0$).

(1) $\Delta H = \Delta U = 0$ for expansion of gas from one bulb to another bulb connected by stopcock.

(2) Endothermic processes – i.e. melting of ice at $T > 0^\circ\text{C}$, $\Delta_{\text{fus}}H^0 = +6 \text{ kJ mol}^{-1}$.

Thus increasing disorder and lowering energy are 2 factors in spontaneous processes.

Entropy (S) is the state function that is a measure of disorder.

$$dS = \frac{dq_{\text{rev}}}{T} \quad (1)$$

dq_{rev} is the differential reversible heat, small heat change for a reversible process (only slightly perturbed from equilibrium, i.e. $T_{\text{system}} \sim T_{\text{surrounding}}$). S is a state function, thus its cyclic integral should vanish since the final & initial states are the same for such an integral.

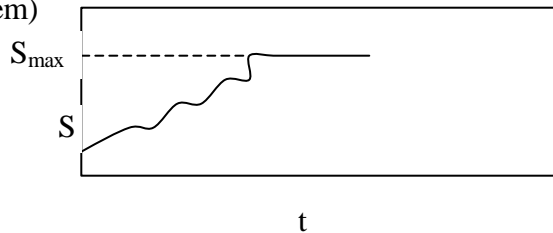
$$\oint dS = \oint \frac{dq_{\text{rev}}}{T} = 0 \quad (2)$$

To find ΔS for irreversible transformation, we are in essence finding ΔS for the reversible transformation for the same initial and final states.

2nd Law of Thermodynamics: The Entropy of the universe is increasing: $\Delta S_{\text{universe}} > 0$

1. Any spontaneous change occurring in an isolated system is attended by an increase in entropy of the system. ($dS > 0$ at for isolated system not at equilibrium)

2. Entropy of an isolated system has a maximum value at equilibrium. ($dS = 0$ at equil for isolated system)



For any process $dS = dS_{\text{prod}} + dS_{\text{exchange}}$

$$dS = dS_{\text{prod}} + \frac{dq}{T}$$

For a reversible process the above equation: $dS = \frac{dq_{\text{rev}}}{T}$ since $dS_{\text{prod}} = 0$

For an irreversible process: $dS = dS_{\text{prod}} + \frac{dq_{\text{irr}}}{T}$ since $dS_{\text{prod}} > 0$

Thus for an irreversible process: $dS > \frac{dq_{\text{irr}}}{T}$

These may be stated together as the Clausius Inequality:

$$dS \geq \frac{dq}{T} \quad (3)$$

II. Boltzmann-Planck Equation: $S = k \ln w$

Boltzmann-Planck Equation

In a spontaneous process the probability increases and S increases then S and W (# of complexions = statistical weight prop to probability) are related $S=f(W)$.

W = the number of ways we can have an ensemble state with a_1 systems in state 1, a_2 in 2, etc of an ensemble consisting of A distinguishable systems:

$$W(a_1, a_2, a_3, \dots) = \frac{A!}{a_1! a_2! a_3! \dots} \quad (4)$$

For example if we have 5 distinguishable systems located at 5 positions with two systems with energy 1: $a_1 = 2$, and 3 with energy 2, $a_2 = 3$.

$$W(2,3) = \frac{5!}{2!3!} = 10 \text{ This corresponds to simply placing } a_1 \text{ at any two positions and } a_2 \text{ will}$$

automatically occupy remaining:

$a_1 a_1 a_2 a_2 a_2$ $a_1 a_2 a_1 a_2 a_2$ $a_1 a_2 a_2 a_1 a_2$ $a_1 a_2 a_2 a_2 a_1$
 $a_2 a_1 a_1 a_2 a_2$ $a_2 a_1 a_2 a_1 a_2$ $a_2 a_1 a_2 a_2 a_1$
 $a_2 a_2 a_1 a_1 a_2$ $a_2 a_2 a_1 a_2 a_1$
 $a_2 a_2 a_2 a_1 a_1$

Consider 2 systems having entropies S_A and S_B , with statistical weights W_A and W_B . If the systems are combined the probability of the resulting system is the product $W_A \times W_B$ whereas the entropy being additive is the sum $S_A + S_B$. Hence $S_{AB} = S_A + S_B = f(W_A \times W_B)$ since $S_A = f(W_A)$ and $S_B = f(W_B)$ it follows

$f(W_A) + f(W_B) = f(W_A \times W_B)$ logarithms are such a function that do this

$$S = k \ln W \quad (5)$$

Boltzmann-Planck Equation: most famous equation in statistical thermodynamics.

At equilibrium S is at a maximum and Ω is at a max, and all a_j are equal (probability is broadly distributed), thus $A = n\Omega$, let $a_j = n \Omega(E)$ is the degeneracy associated with energy E of a state of the ensemble. Inserting Eq. 4 into Eq. 5

$$S_{ensemble} = k \{ \ln A! - [\ln a_1! + \ln a_2! + \ln a_3! + \dots] \} \quad (6)$$

Stirling's Approximation: $\ln N! = N \ln N - N$

$$S_{ensemble} = k \{ A \ln A - A - [a_1 \ln a_1 - a_1 + a_2 \ln a_2 - a_2 + a_3 \ln a_3 - a_3 + \dots] \} \quad (7)$$

$$\text{but } nW = A \quad n = a_j \quad (8)$$

Inserting Eq. 8 into 7

$$S_{ensemble} = k \left\{ \sum_{j=1}^W nW \ln nW - nW - \sum_{j=1}^W a_j \ln a_j - \sum_{j=1}^W a_j \right\} \quad (9)$$

$$S_{ensemble} = k \left\{ \sum_{j=1}^W nW \ln nW - nW - \sum_{j=1}^W a_j \ln n - \sum_{j=1}^W a_j \right\} = k \{ nW \ln nW - nW - [nW \ln n - nW] \}$$

$$S_{ensemble} = k \{ n\Omega \ln n\Omega - \Omega n \ln n \} \quad (11)$$

$$S_{ensemble} = knW \{ \ln nW - \ln n \} = knW \ln \frac{nW}{n} = kn\Omega \ln \Omega \quad (12)$$

But $S_{ensemble} = AS_{system} = n\Omega S_{system} \rightarrow S_{system} = S_{ensemble} / n\Omega$
 $S = k \ln W \quad (13)$

Example: For a system of N distinguishable spins or dipoles, the degeneracy is 2^N since each dipole or spin may have 2 orientations. So $S = k_B \ln 2^N = Nk_B \ln 2$