

## Entropy

Following the discussion in Kittel (1969), entropy is proportional to the logarithm of the number of accessible states,  $g$ , available to the thermodynamic system. We define  $\sigma$  as the natural logarithm of the number of accessible states,  $g$ .

$$\sigma = \log(g)$$

Note that  $\sigma$  is dimensionless.

Entropy is additive. If the number of accessible states of two systems are  $g_1$  and  $g_2$  respectively, then the total number of accessible states available to the two systems is  $g_1 g_2$  and

$$\sigma = \log(g_1 g_2) = \log(g_1) + \log(g_2) = \sigma_1 + \sigma_2$$

To understand this, consider two systems. The first has 3 possible states, 1a, 1b and 1c and the second has 2 possible states, 2a and 2b. The total possible set of states is

$$(1a,2a); (1a,2b); (1b,1a); (1b,2b); (1c,2a); (1c,2b)$$

So there are 6 possible states which is  $3 \times 2 = g_1 g_2$ .

**Equilibrium** is defined as when the combined system achieves its most probable state. This turns out to be the state where the product of the number of the two accessible state is maximum,

$$g_{max} = \max(g_1 g_2)$$

Since entropy is the logarithm of the number of accessible states, this also means entropy will be maximum at equilibrium.

Temperature is related to entropy as

$$\frac{1}{k_B T} = \left( \frac{\partial \sigma}{\partial U} \right)_N$$

where  $U$  is the energy of the system,  $T$  is the temperature of the system and  $N$  is the number of molecules in the system. Moving Boltzmann's constant to the numerator of the other side we start to see the more familiar form of the relation between entropy and energy

$$\frac{1}{T} = \left( \frac{\partial k_B \sigma}{\partial U} \right)_N = \left( \frac{\partial S}{\partial U} \right)_N$$

where  $S = k_B \sigma$ .  $S$  (rather than  $\sigma$ ) is the form of entropy used in atmospheric science. There is also  $s = S/N$  which is the entropy per molecule in the system.

$$dS|_{N=const} = \left( \frac{\partial S}{\partial U} \right)_N dU = \frac{dU}{T} = \frac{dQ}{T}$$

Entropy tends to either remain the same or increase. We can see this from the following example. We bring two systems in contact with one another, one hot and one cold. The hot one (System 1) will transfer energy to the cold one (System 2).

$$dS = \left( \frac{\partial S_1}{\partial U_1} \right)_{N_1} (-dU) + \left( \frac{\partial S_2}{\partial U_2} \right)_{N_2} (dU) = \left( -\frac{1}{T_1} + \frac{1}{T_2} \right) dU$$

Since  $T_1 > T_2$ ,  $(T_2)^{-1} > (T_1)^{-1}$  and  $dS > 0$ . In general,  $dS \geq 0$ . In fact, only when the temperatures of the two systems are equal *before* they are put in thermal contact will the entropy of the combined two systems remain unchanged after contact.

Note: when the two systems are brought into thermal contact, their *initial* entropy is lower than their final entropy when the two temperatures become equal.