

# Entropy

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## Entropy

The equilibrium state for a system corresponds to the value of  $\alpha$  for which  $\Omega(E, V, N, \alpha)$  attains its maximum value with  $E, V, N$  fixed. The equilibrium state is the state of maximum probability.

Instead of using  $\Omega$ , we will now introduce the entropy  $S$  as a measure of the disorder of the system. The entropy of the system is given by

$$S = k \ln \Omega(E, V, N, \alpha).$$

During real (as distinct from idealized reversible processes) the entropy of an isolated system always increases. In the state of equilibrium, entropy attains its maximum value.

This is the Clausius statement of the second law of thermodynamics. At this time, I am going to use the maximization of  $\Omega$  to derive the concepts of temperature, pressure, and chemical potential.

## Thermal Equilibrium

$E_1$	$E_2$
$V_1$	$V_2$
$N_1$	$N_2$

Consider a system, that is isolated, and is divided into two parts by a wall s.t.

$$E_1 + E_2 = E$$

$$V_1 + V_2 = V$$

$$N_1 + N_2 = N$$

These equations are called the equations of constraint. We'll further assume that the sub-systems are not in equilibrium and that the wall separating them is rigid, impermeable and diathermal. That is, energy can pass through the wall,

particles cannot, and the wall is fixed in place. For each division of  $E, V$ , and  $N$  between the sub-systems specified by the equations above, we can write

$$\Omega(E, V, N, \underbrace{E_1, V_1, N_1}_{\alpha}) = \Omega_1(E_1, V_1, N_1) \Omega_2(E_2, V_2, N_2)$$

where  $\Omega_1$  is the multiplicity of sub-system 1 in the macrostate specified by  $(E_1, V_1, N_1)$ ,  $\Omega_2$  is the multiplicity of sub-system 2 in the macrostate specified by  $(E_2, V_2, N_2)$ , and  $\Omega$  is the multiplicity of the composite system with this division of energy, volume, and particle number. Taking the product of  $\Omega_1$  and  $\Omega_2$  is justified by the fundamental principle of counting. The constraint equations limit  $E_1, E_2$  etc., we're choosing  $E_1, V_1$ , and  $N_1$  as independent - in other words, they correspond to the  $\alpha$  that we used earlier. But  $S = k \ln \Omega$ , so

$$S(E, V, N, E_1, V_1, N_1) = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2).$$

Now let the sub-systems come to equilibrium, at equilibrium, entropy is maximized, therefore

$$dS = 0,$$

and

$$0 = dS_1 + dS_2$$

we can rewrite this as

$$0 = \frac{\partial S_1}{\partial E_1} dE_1 + \frac{\partial S_1}{\partial V_1} dV_1 + \frac{\partial S_1}{\partial N_1} dN_1 + \frac{\partial S_2}{\partial E_2} dE_2 + \frac{\partial S_2}{\partial V_2} dV_2 + \frac{\partial S_2}{\partial N_2} dN_2$$

Now using our equations of constraint  $dV_1 = dV_2 = dN_1 = dN_2$  and  $dE = 0$ , so  $dE_1 = -dE_2$ , we can simplify this expression to

$$0 = \left( \frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} dE_1 + \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} dE_2$$

and using  $dE_1 = -dE_2$ , this becomes

$$\left( \frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} = \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2}.$$

This is the condition for thermal equilibrium (i.e. no heat transfer). We already know a condition for the equilibrium of two systems in thermal contact:

$$T_1 = T_2.$$

We use this to define absolute temperature,

$$\frac{1}{T_i} = \left( \frac{\partial S_i}{\partial E_i} \right)_{V_i, N_i}.$$

The choice is not unique, but it this choice makes the absolute temperature scale identical to the ideal gas temperature scale.

## Thermal and Mechanical Equilibrium

We will now consider two subsystems not in equilibrium separated by moveable, diathermal, impermeable walls. In such a system, energy and volume will flow until equilibrium is achieved.

$E_1$	$E_2$
$V_1$	$V_2$
$N_1$	$N_2$

The equations of constraint are

$$E_1 + E_2 = E,$$

$$V_1 + V_2 = V,$$

$$N_1 + N_2 = N.$$

These yield  $dE_1 = -dE_2$ ,  $dV_1 = -dV_2$ , and  $dN_1 = dN_2 = 0$ . Again we use entropy maximization at equilibrium,  $dS = 0$  yielding

$$0 = \left( \frac{\partial S_1}{\partial E_1} \right) dE_1 + \left( \frac{\partial S_1}{\partial V_1} \right) dV_1 + \left( \frac{\partial S_2}{\partial E_2} \right) dE_2 + \left( \frac{\partial S_2}{\partial V_2} \right) dV_2$$

At equilibrium, we would expect temperature and pressure to be equal in this case.

$$0 = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left[ \left( \frac{\partial S_1}{\partial V_1} \right) - \left( \frac{\partial S_2}{\partial V_2} \right) \right] dV_1$$

Thus at equilibrium,  $T_1 = T_2$ , and  $\left( \frac{\partial S_1}{\partial V_1} \right)_{E_1, N_1} = \left( \frac{\partial S_2}{\partial V_2} \right)_{E_2, N_2}$ . Now the partial derivatives in this case must describe the equality of pressure. We define pressure for each subsystem as

$$\frac{p_i}{T_i} = \left( \frac{\partial S_i}{\partial V_i} \right)_{E_i, N_i}.$$

This definition reduces to  $pV = NkT$  when applied to an ideal gas.

## Thermal and Diffusive Equilibrium

We can continue this analysis in a similar vein by considering the wall to be diathermal, rigid and permeable. The analysis leads to an expression for the equilibrium of matter flow. This leads to the definition of chemical potential  $\mu_i$  of the  $i^{\text{th}}$  chemical species through

$$\left( \frac{\partial S_i}{\partial N_i} \right) = -\frac{\mu_i}{T_i}.$$

Chemical potential controls matter equilibrium.

## The Fundamental Thermodynamic Relation

$S = S(E, V, N)$  contains complete thermodynamic information. We could equivalently write  $E = E(S, V, N)$ ,  $E$  is minimized at equilibrium, if we start from  $E$ , and consider the same systems and walls we get the following definitions:

$$T_i = \left( \frac{\partial E_i}{\partial S_i} \right)_{V_i, N_i}$$

$$p_i = - \left( \frac{\partial E_i}{\partial V_i} \right)_{E_i, N_i}$$

$$\mu_i = \left( \frac{\partial E_i}{\partial N_i} \right)_{S_i, V_i}$$

Thus if  $E = E(S, V, N)$ , then

$$dE = \left( \frac{\partial E}{\partial S} \right)_{V, N} dS + \left( \frac{\partial E}{\partial V} \right)_{S, N} dV + \left( \frac{\partial E}{\partial N} \right)_{S, V} dN$$

and

$$dE = TdS - pdV + \mu dN$$

This is called the fundamental thermodynamic relation or the fundamental thermodynamic identity. Note:  $T = T(S, V, N)$ ,  $p = p(E, V, N)$ , and  $\mu = \mu(N, S, V)$ . The fundamental thermodynamic relation can be used to recover the definitions of  $T, p, \mu$ . We can also solve the relationship for entropy

$$dS = \frac{dE}{T} + \frac{p}{T}dV - \frac{\mu}{T}$$

this allows us to recover the equivalent definitions in the entropy representation.

In general there is more than a single chemical species in our thermal system. The general form of the fundamental thermodynamic relation is:

$$dE = TdS - pdV + \sum_j \mu^j dN^j$$

where  $\mu^j$  is the chemical potential of the  $j^{th}$  chemical species. In this expression  $\mu^j = (\partial E^j / \partial N^j)_{S, V, \mu^i}$ , and the equilibrium condition is  $\mu_1^j = \mu_2^j$ .  $\mu$  is a potential for matter flow. At this point, we are in a good position to explore entropy and equilibrium.

## Entropy and Equilibrium

$S = S(E, V, N)$  is a fundamental relation in that it contains complete thermodynamic information about the system. At equilibrium  $S$  is a maximum.

The properties of  $S$  are that  $S = \sum S_i$  is a continuous, differentiable, monotonic function of  $E$  that is homogeneous of degree one in  $E$ ,  $V$ , and  $N$ . For now we will also assert that at  $T = 0$ ,  $S = 0$ . This latter statement assumes the strong form of the third law of thermodynamics. We will explore the strong and weak forms of the third law of thermodynamics at a later date.

## Equilibrium in the Entropy Representation

Consider again two subsystems separated by rigid, impermeable, diathermal walls.

$$\begin{aligned} S &= S_1 + S_2 \\ dS &= \left( \frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} dE_1 + \left( \frac{\partial S_2}{\partial E_2} \right)_{V_2, N_2} dE_2 \\ dS &= \frac{1}{T_1} dE_1 + \frac{1}{T_2} dE_2 \end{aligned}$$

Now, at equilibrium  $dE = 0$  and  $dS = 0$ , and  $T_1 = T_2$ . Close to equilibrium we can write

$$dS \approx \underbrace{\left( \frac{1}{T_1} - \frac{1}{T_2} \right)}_{(-)ve} dE_1.$$

Assuming  $T_1 > T_2$  by a small amount we can see that since  $dS$  must be positive,  $dE_1$  must be negative. In other words if  $T_1 > T_2$ ,  $E_1$  will decrease,  $E_2$  will increase as energy flows from subsystem one to subsystem two. Thus our new formulation agrees with our intuitive understanding of the situation.

Now if we change the wall to having a moveable, impermeable diathermal wall, we have

$$dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dE_1 + \left( \frac{p_1}{T_1} - \frac{p_2}{T_2} \right) dV_1.$$

Now,  $E$  and  $V$  are independent, so the coefficients must separately equal 0. Thus, as we have noted, at equilibrium  $T_1 = T_2$  and  $p_1 = p_2$ . Infinitesimally close to 0, we can write

$$\underbrace{dS}_{(+)ve} \approx \underbrace{\frac{p_1 - p_2}{T}}_{(+)ve} \underbrace{dV_1}_{(+)ve},$$

where I have assumed that  $p_1 > p_2$ . This again agrees with our intuitive understanding of the situation — the region at higher pressure will grow. We could similarly analyze the situation of a rigid, permeable, diathermal wall. Infinitesimally close to equilibrium we would find that

$$\underbrace{dS}_{(+)ve} \approx \underbrace{\frac{\mu_2 - \mu_1}{T}}_{(-)ve \text{ if } \mu_1 > \mu_2} \underbrace{dV_1}_{(-)ve}$$

matter flows from high  $\mu$  to low  $\mu$ .

## Entropy and the Energy Transfer by Heating

Entropy increases can also be related to the energy transfer by heating. We could for instance (as our author does, and you should read) examine entropy changes as energy is transferred to an ideal gas by heating. Other examples are to be found in your university physics text. In general, we find that

$$\Delta S_{\text{system}} \geq \frac{\text{Energy transfer by heating}}{T}.$$

The equality holds for a *quasistatic* process — in other words for a slow process where the system remains arbitrarily close to equilibrium. For fast processes, the entropy change is greater. We have to be careful to use the appropriate temperature, for slow processes, there is no problem, the system and the heating source will have the same temperature. For fast processes the system is far from equilibrium, the system temperature could change drastically. For fast processes, the appropriate temperature to use is the temperature of the heating source.

Before looking at some examples, let's remind ourselves of a few basic facts. Recall the first law, we have written it in the form  $\Delta E = Q - W$ , where  $W$ , and  $Q$  are not functions of state. We can write this for infinitesimals as  $dE = \bar{d}Q - \bar{d}W$  where the  $\bar{d}$  denotes an inexact differential. We will frequently integrate such forms, but should remember that they are not true differentials. If you look at the examples, you will see that we are integrating well defined functions or the expressions will contain an integrating factor. As an example  $\frac{1}{T}$  is an integrating factor for  $\bar{d}Q$ . In other words  $dS = \bar{d}Q/T$  is a perfect differential if  $\bar{d}Q$  is added reversibly. We have also defined  $W$  to be positive when the system does work on its environment. To fix how we apply this to problems consider heat expanding a gas in a piston-cylinder arrangement, the work done by the expanding gas is given by  $W = \int_{V_i}^{V_f} p dV$ .

## Examples

It's now time to use some of our tools to examine some specific situations.

### Melting Ice

If ice melts slowly at  $0^\circ\text{C}$ , by how much does its multiplicity change?

$$\Delta S = S_{\text{liquid}} - S_{\text{ice}} = k \ln \Omega_{\text{liquid}} - k \ln \Omega_{\text{ice}} = k \ln \frac{\Omega_{\text{liquid}}}{\Omega_{\text{ice}}}$$

Now, examining this, we can see that we will need to calculate  $\Delta S$ . If we consider the ice to melt slowly (and there is no reason not to make this assumption, the number of accessible microstates is not going to depend on the rate of melting!) So we can write

$$\Delta S = \frac{Q}{T}$$

Since my calculators were all at the office, we'll use our authors numbers, we take 18 g of ice, at 273 K, with  $L_{f_{ice}} = 3.34 \times 10^5 \text{ J/Kg}$ , we get

$$\Delta S = \frac{(3.34 \times 10^5 \text{ J/Kg})(18 \times 10^{-3} \text{ Kg})}{273 \text{ K}} = 22 \text{ J/K}.$$

We can now combine our calculations to yield

$$\ln \frac{\Omega_{liquid}}{\Omega_{ice}} = \frac{1}{k} \frac{Q}{T} = \frac{22 \text{ J/K}}{1.4 \times 10^{-23} \text{ J/K}} = 1.6 \times 10^{24}$$

then

$$\frac{\Omega_{liquid}}{\Omega_{ice}} = e^{1.6 \times 10^{24}} = 10^{6.9 \times 10^{23}}.$$

There are many more microstates available to the liquid than there were to the solid.

## Object thrown into the sea

An object of mass  $m$ , mass specific heat  $c_p$  and temperature  $T_1$  is thrown into the sea which has temperature  $T_0$ . Calculate the total change in entropy. Assume the process is slow.

$$\Delta S_{total} = \Delta S_{mass} + \Delta S_{sea}$$

$$\Delta S_{total} = \int_{\text{mass}} \frac{\mathrm{d}Q}{T} + \int_{\text{sea}} \frac{\mathrm{d}Q}{T}$$

$$\Delta S_{total} = \int_{T_1}^{T_0} \frac{m c_p \mathrm{d}T}{T} + \int \frac{\mathrm{d}Q}{T_0}$$

$$\Delta S_{total} = m c_p \ln \left( \frac{T_0}{T_1} \right) + \frac{Q}{T_0}$$

$$\Delta S_{total} = m c_p \ln \left( \frac{T_0}{T_1} \right) + \frac{\overbrace{m c_p (T_1 - T_0)}^{\text{heat lost by mass} = \text{heat gained by sea}}}{T_0}$$

$$\Delta S_{total} = m c_p \left( \frac{T_1}{T_0} - 1 - \ln \frac{T_1}{T_0} \right)$$

## Isothermal Compression of an Ideal Gas

For an ideal gas, we have noted that  $E = E(T)$  only. Now, recall the first law  $\Delta E = Q - W$ , or in differential form  $dE = \bar{d}Q - \bar{d}W$ . In this case if we consider compression from  $V_1$  to  $V_2$ , at fixed temperature  $dE = 0$ , and  $\bar{d}W = pdV$ , thus

$$dE = \bar{d}Q - pdV.$$

In this case however, since the process is isothermal  $dE = 0$  and so  $\bar{d}Q = pdV$ , then

$$\Delta S = \int_1^2 \frac{\bar{d}Q}{T} = \int_1^2 \frac{pdV}{T} = \frac{1}{T} \int_1^2 pdV$$

now, recall  $pV = NkT$ , so

$$\Delta S = \int_1^2 \frac{NkdV}{V} = Nk \ln \frac{V_2}{V_1} = -Nk \ln \frac{V_1}{V_2}.$$

## Entropy and Disorder

We have defined entropy in terms of the logarithm of the multiplicity. Sometimes entropy is described as a measure of disorder, the greater the disorder, the greater the entropy. This works well if we are only considering solids, liquids, and gases. You should be aware that it is not always a good description and should be used with caution.