

Entropy

Thermodynamic results

Most important things about entropy:

Entropy is a state variable.

In an infinitesimal, quasi-equilibrium process, the entropy change of a system is

$$dS = dQ/T.$$

Second Law:

For any process in an *isolated* system, $\Delta S \geq 0$.

(Equality holds for reversible processes.)

Thus, if an isolated system has a macroscopic variable that is free to change, equilibrium in that variable will be obtained when it takes the value that maximizes the entropy.

Considering S as a function of U and V and using $dS=dQ/T$, we can show that

$$\left. \frac{\partial S}{\partial U} \right|_V = \frac{1}{T} \quad \text{and} \quad \left. \frac{\partial S}{\partial V} \right|_U = \frac{P}{T}$$

(These last relations are not in the text, but you should know them.)

There are a few important results that follow from the fact that entropy is a state variable and that $dS=dQ/T$ for quasi-equilibrium processes.

Entropy change for each of the four basic thermodynamic processes.

Entropy change for a free expansion.

How the second law in the version above determines the direction of heat flow

How the second law in the version above limits the efficiency of heat engines.

How to exploit the fact that entropy is a state variable to calculate entropy changes in irreversible processes.

Partial derivatives of the entropy

We will now show that

$$\left. \frac{\partial S}{\partial U} \right|_V = \frac{1}{T} \quad \text{and} \quad \left. \frac{\partial S}{\partial V} \right|_U = \frac{P}{T}$$

Considering S as a function of U and V , i.e. $S(U,V)$, from calculus we have

$$dS = \left. \frac{\partial S}{\partial U} \right|_V dU + \left. \frac{\partial S}{\partial V} \right|_U dV .$$

At the same time, we have

$$dS = \frac{dQ}{T} = \frac{dU + dW}{T} = \frac{dU + PdV}{T} = \frac{1}{T} dU + \frac{P}{T} dV$$

In comparing these two expressions for dS , we can equate the two versions of the factors multiplying dU and dV , respectively, to obtain the desired relations.

Statistical mechanical view of entropy:

Microstates and macrostates:

Macrostate: a specification of the system that gives definite values to the macroscopic state variables, e.g. P , V , T , U .

Microstate: a complete description of the system that specifies the values of all the microscopic variables at the atomic level.

In most cases, for macroscopic systems, there are a huge number of microstates consistent with a given macrostate. This multiplicity of microstates is called w . Generally, the number of microstates is a steeply increasing function of both the internal energy U and the size of the system, e.g. the number of molecules or the number of degrees of freedom. Let's illustrate this with a toy model.

Toy model

This can be thought of as an extreme simplification of a quantum mechanical model of a solid crystal of atoms such as table salt. We need to consider quantum mechanics in at least a very basic way because a classical model will always give infinity for the entropy. So we will consider N atoms in the solid. Each atom can oscillate in each of the three directions of space, so there are $M=3N$ modes of oscillation into which to put energy. The quantum mechanics comes in by saying the energy is quantized and comes in units of a finite size ε . Here is the notation:

N = number of atoms

$M = 3N$ = number of modes

$i = 1, 2, 3, \dots, M$ = mode label

ε = energy unit

n_i = number of units of energy in mode i

$$U = \sum_{i=1}^M \varepsilon n_i = \text{total energy}$$

$$n = \frac{U}{\varepsilon} = \sum_{i=1}^M n_i$$

U is a macroscopic state variable. Knowledge of U specifies a macrostate. Knowledge of all the n_i specifies a microstate—the exact way that the energy is arranged among the modes. There are many ways to do this (many microstates) that all give the same U (the same macrostate). The notation is $w(N,U)$ for the number of microstates that give the same macrostate. This is also called the multiplicity. It depends on the macrostate, which is specified by giving the number of atoms N and the total energy U . It will turn out that in our toy model and in typical real systems, w is a very steeply increasing function of both N and U . Those general properties are much more important than exactly how it works out in our model.

For a very small system, with $N=1$, $M=3$, and $U=2\varepsilon$, we can easily list all the possibilities for putting two identical things in three slots.

2	0	0
1	1	0
1	0	1
0	2	0
0	1	1
0	0	2

The general formula for this toy model is

$$w(N,U) = \frac{(M-1+n)!}{n!(M-1)!} \text{ with } M = 3N \text{ and } U = n\varepsilon .$$

The only important aspect of this formula is that it is a steeply rising function of N and U or, equivalently, M and n.

Now consider thermal interaction between two such systems A and B. Via heat flow, they can exchange energy and share a fixed total amount of energy $U = U_A + U_B$. For a specific example, let's do $N_A = 1$, $M_A = 3$ and $N_B = 2$, $M_B = 6$. I will take them to be sharing nine units of energy. So $n = 9$, and $U = 9\varepsilon$. We can then use the formula for w to construct the following table.

n_A	n_B	w_A	w_B	$w_{AB} = w_A w_B$
0	9	1	2002	2002
1	8	3	1287	3861
2	7	6	792	4752
3	6	10	462	4620
4	5	15	252	3780
5	4	21	126	2646
6	3	28	56	1568
7	2	36	21	756
8	1	45	6	270
9	0	55	1	55

The first two columns give the macrostates of A and B. The next two columns give the multiplicity for those macrostates. Note that as the energy increases or as the number of modes increases, the multiplicity

increases. The last column gives the multiplicity of the combined system for the given sharing of the total energy. A given sharing of the energy is called a macropartition of the energy. Each row is a different macropartition of the total energy between the two systems. The multiplicity for the combined system is relatively small when one or the other has too much of the energy and has a peak in the middle when the sharing is not too extreme.

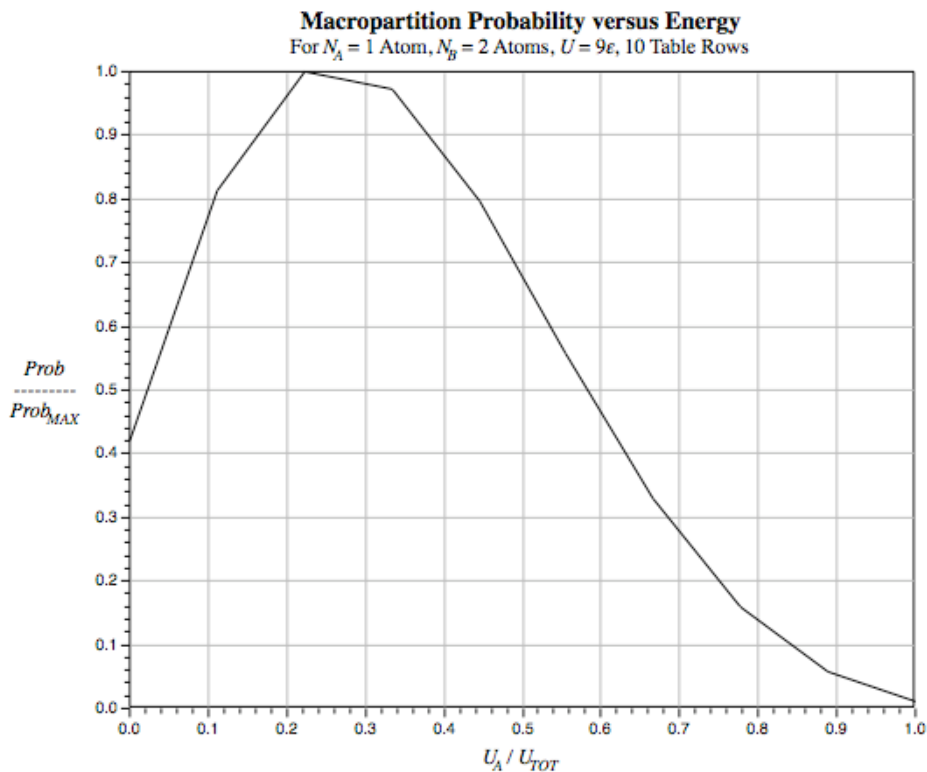
So far, all of this is just counting. Where's the physics? That comes from the key input called the fundamental assumption:

Fundamental assumption (microcanonical distribution):

An isolated system is equally likely to be in any of its accessible microstates.

From that, it follows immediately that the probability of a given macropartition is proportional to the joint multiplicity, *i.e.*

$$P(U_A, U_B) \propto W_{AB} .$$



Let's see what happens as we increase the system size and the amount of energy. Here is $N_A=4$, $N_B=5$, $n=30$. (The Omega in the table heading is the same as w.)

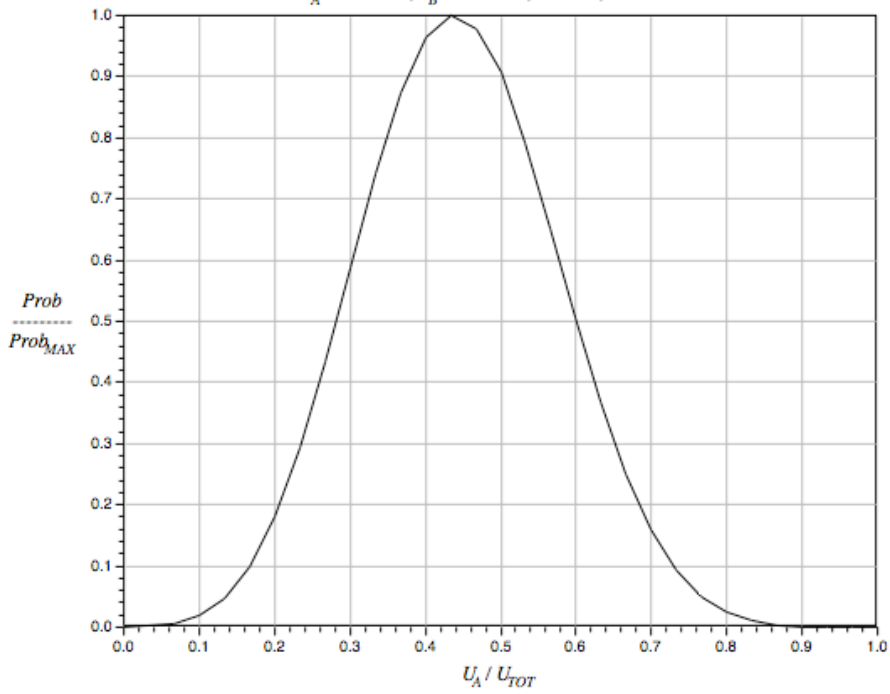
Number of atoms in System A = 4
 Number of atoms in System B = 5
 Total combined system energy = 30 units.

U(A)	U(B)	Omega(A)	Omega(B)	Omega(AB)	Fraction of states
0	30	1	1.150e+11	1.150e+11	1.73e-5
1	29	12	7.838e+10	9.405e+11	0.00014*
2	28	78	5.286e+10	4.123e+12	0.00062*
3	27	364	3.524e+10	1.283e+13	0.00193*
4	26	1,365	2.321e+10	3.168e+13	0.00477*
5	25	4,368	1.508e+10	6.589e+13	0.00991*
6	24	12,376	9.670e+9	1.197e+14	0.01801*
7	23	31,824	6.107e+9	1.944e+14	0.02924*
8	22	75,582	3.796e+9	2.869e+14	0.04317*
9	21	167,960	2.320e+9	3.897e+14	0.05863*
10	20	352,716	1.392e+9	4.910e+14	0.07387*
11	19	705,432	818,809,200	5.776e+14	0.08691*
12	18	1,352,078	471,435,600	6.374e+14	0.09590*
13	17	2,496,144	265,182,525	6.619e+14	0.09959*
14	16	4,457,400	145,422,675	6.482e+14	0.09753*
15	15	7,726,160	77,558,760	5.992e+14	0.09016*
16	14	13,037,895	40,116,600	5.230e+14	0.07869*
17	13	21,474,180	20,058,300	4.307e+14	0.06481*
18	12	34,597,290	9,657,700	3.341e+14	0.05027*
19	11	54,627,300	4,457,400	2.435e+14	0.03664*
20	10	84,672,315	1,961,256	1.661e+14	0.02499*
21	9	129,024,480	817,190	1.054e+14	0.01586*
22	8	193,536,720	319,770	6.189e+13	0.00931*
23	7	286,097,760	116,280	3.327e+13	0.00501*
24	6	417,225,900	38,760	1.617e+13	0.00243*
25	5	600,805,296	11,628	6.986e+12	0.00105*
26	4	854,992,152	3,060	2.616e+12	0.00039*
27	3	1.203e+9	680	8.183e+11	0.00012*
28	2	1.676e+9	120	2.011e+11	3.03e-5
29	1	2.312e+9	15	3.468e+10	5.22e-6
30	0	3.159e+9	1	3.159e+9	4.75e-7

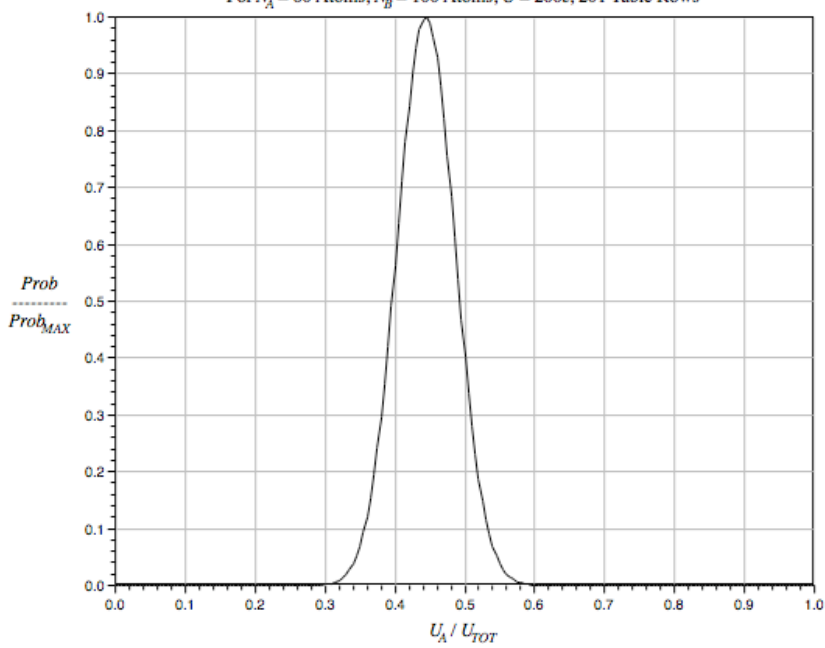
Total number of microstates: 6.646e+15

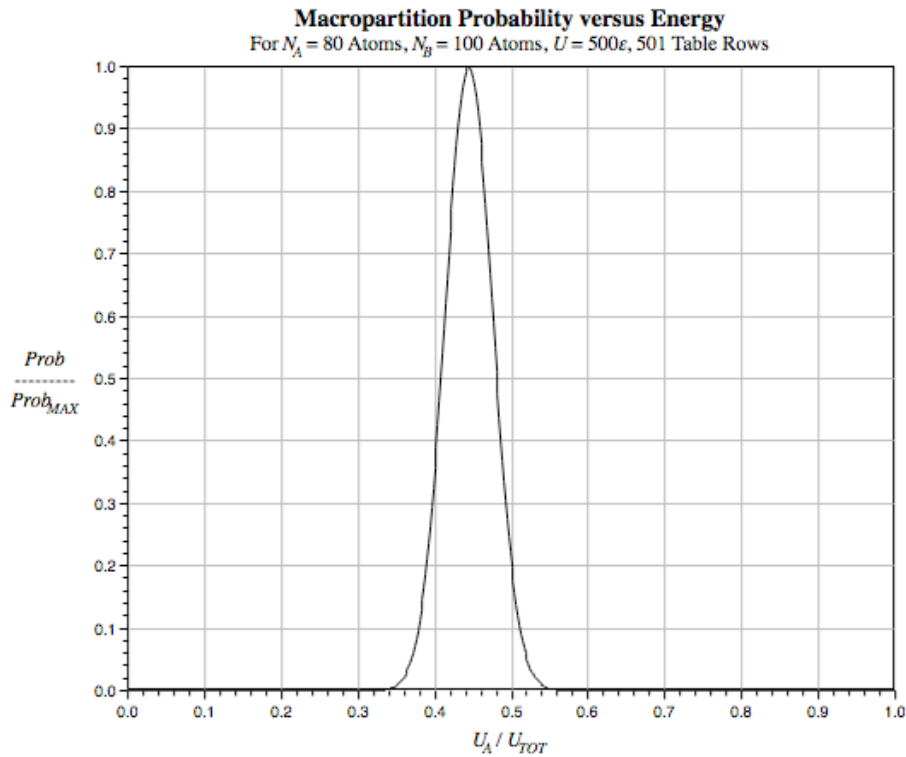
Now the multiplicities are much steeper and their product is more sharply peaked. This trend continues for further increases of the N or n.

Macropartition Probability versus Energy
For $N_A = 4$ Atoms, $N_B = 5$ Atoms, $U = 30\epsilon$, 31 Table Rows



Macropartition Probability versus Energy
For $N_A = 80$ Atoms, $N_B = 100$ Atoms, $U = 200\epsilon$, 201 Table Rows

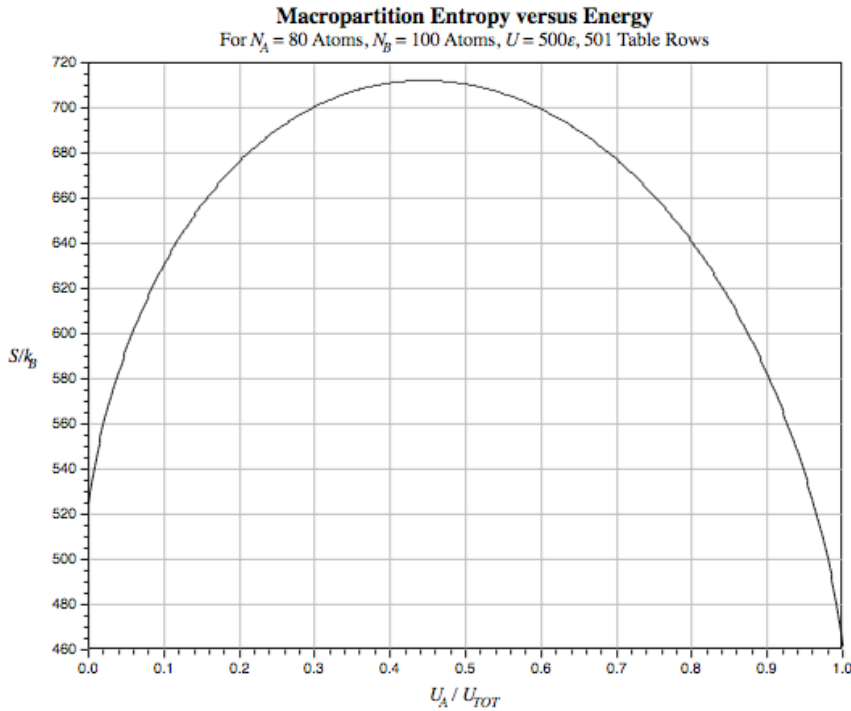




Since the numbers increase so rapidly, it is more convenient to deal with the natural log and thus with a function that is additive rather than multiplicative when systems are combined. That is the entropy. With w the number of microstates available to the system in a given macrostate, the statistical mechanical definition of the entropy of that macrostate is

$$S = k \ln w \quad \text{or} \quad w = e^{S/k} .$$

For our combined system with total energy U_{AB} ,
 $S_{AB}(U_A) = k \ln(w_A w_B) = S_A(U_A) + S_B(U_B) = S_A(U_A) + S_B(U_{AB} - U_A)$



For a system with a large number M of degrees of freedom and many units ϵ of energy per degree of freedom $U/(\epsilon M)$, the behavior of the multiplicity above is $w = \left(\frac{U}{\epsilon M}\right)^M$, which is typical of real systems. This

has the properties of growing rapidly with both U and M . For a pair of such systems in thermal interaction and sharing a total energy U ,
 $w_{AB}(U_A) = w_A(U_A)w_B(U_{AB} - U_A)$.

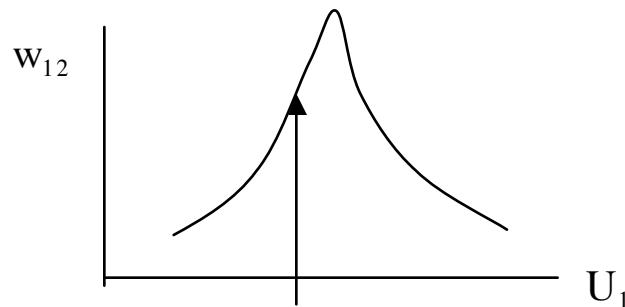
The first factor grows rapidly with U_A while the second falls. The product increases to a peak and then decreases.

General statements

For a combined system with two parts 1 and 2, the multiplicity is the product $w_{12} = w_1 w_2$, and the entropy is $S_{12} = S_1 + S_2$. If the two systems are in interaction and have macroscopic quantities that are free to vary such as $U = U_1 + U_2$, a macropartition is specified by giving the values of the macrovariables, e.g. U_1 and U_2 . Generally w_{12} and S_{12} are *very strongly* peaked functions of the macroscopic variables that specify a macropartition.

Thus the probability of a macropartition is proportional to its multiplicity $P \propto w = e^{S/k}$. The macropartition with the most

microstates is the most likely macropartition, and it is the one that maximizes the entropy.



Since the maximum of this graph is the macropartition with the most microstates, it is (by the fundamental assumption) the most likely macropartition. If the system is away from the maximum as indicated by the arrow, there will be more microstates if it moves to the right toward the maximum. Thus the system will be most likely to move toward the maximum and then stay near it. This is the approach to thermal equilibrium. Thus the equilibrium division of energy (the macropartition) is determined by finding the value of $U_1 = U_{MAX}$ at the maximum of w_{12} .

For the combined system, $S_{12}(U_1) = S_1(U_1) + S_2(U_2)$, and we find the maximum via

$$0 = \frac{\partial S_{12}(U_1)}{\partial U_1} = \frac{\partial S_1(U_1)}{\partial U_1} + \frac{\partial S_2(U - U_1)}{\partial U_1} = \frac{\partial S_1(U_1)}{\partial U_1} - \frac{\partial S_2(U_2)}{\partial U_2}$$

We can calculate the width of the peak by looking at the ratio of the probability to be a little away from the peak to the probability to be at the peak:

$$\frac{P(U_1 = U_{MAX} + \Delta U)}{P(U_1 = U_{MAX})} = e^{[S_{12}(U_1 = U_{MAX} + \Delta U) - S_{12}(U_1 = U_{MAX})] / k}$$

For the particular form of w above, we can get S and do the calculation of the exponent for small ΔU . The result is

$$\frac{P(U_1 = U_{MAX} + \Delta U)}{P(U_1 = U_{MAX})} = e^{-M \left(\frac{\Delta U}{U_{MAX}}\right)^2}$$

For a macroscopic system, M is *huge*, so the peak is *very narrow*. This result is valid beyond the model that we used to illustrate it. It is essentially the Second Law. The overwhelming probability in a macroscopic system with a huge number of degrees of freedom is to move toward the macropartition that maximizes the entropy and then stay very near it. In this process, entropy increases to its maximum.

Statistical mechanics definition of temperature

Applying these ideas to the case of two systems that can share energy via heat transfer led to the conclusion that maximum entropy and equilibrium comes when

$$\frac{\partial S_1(U_1)}{\partial U_1} = \frac{\partial S_2(U_2)}{\partial U_2}$$

When that is viewed in light of the thermodynamic relation for the partial derivative of entropy with respect to energy, it motivates the statistical mechanical definition of temperature

$$\frac{\partial S}{\partial U} = \frac{1}{T}$$

Entropy of an ideal gas

There are an infinite number of ways to get the entropy of an ideal gas up to an overall constant from thermodynamic relations. To get the overall constant, which we will not do, it is necessary to use a microscopic quantum mechanical model. To get the entropy, we will integrate dS from a reference point to the desired point. Since entropy is a state function, each of the infinite number of paths to use for the integration will give the same answer. Here is a way to do it by integrating S(U,V) in the U,V plane.

We will use

$$\left. \frac{\partial S}{\partial U} \right|_V = \frac{1}{T} \quad \text{and} \quad \left. \frac{\partial S}{\partial V} \right|_U = \frac{P}{T} \quad \text{and} \quad U = (f/2) nR T \quad \text{and} \quad PV = nR T$$

Recall that f is the number of degrees of freedom for a molecule of the gas. For example, $f = 3$ for a monatomic gas or $f = 5$ for a diatomic gas with translations and rotations but no vibrations. We can rewrite the relation between U and T in the form $(1/T) = (f/2) nR /U$ and use that to replace T in the expression for dS . Using the equation of state, we can also replace (P/T) by nR/V . So

$$dS = \left. \frac{\partial S}{\partial U} \right|_V dU + \left. \frac{\partial S}{\partial V} \right|_U dV = \frac{1}{T} dU + \frac{P}{T} dV = \frac{f}{2} nR \frac{dU}{U} + nR \frac{dV}{V}$$

The reference point will be an arbitrary point U_0, V_0 in the U, V plane. The integration path will have two straight-line legs. In the first, $U_0 \rightarrow U$ with V fixed at V_0 , and in the second, $V_0 \rightarrow V$ with U fixed at U . Thus for the first leg, only the first term in dS contributes, and in the second leg, only the second term contributes. That gives

$$S(U, V) = \frac{f}{2} nR \ln \frac{U}{U_0} + nR \ln \frac{V}{V_0} + S_0$$

The integration constant (the entropy at the reference point) is independent of U and V . It can depend on n . However since the entropy must be proportional to n , we can write $S_0 = nR \ln(c)$, with c an unknown numerical constant. Finally, combining all the logs together we have

$$S(U, V) = nR \ln \left[c \left(\frac{U}{U_0} \right)^{f/2} \frac{V}{V_0} \right].$$

Equation of state and $U(T, V)$ from $S(U, V)$

Suppose that we have the entropy as a function of U and V , $S(U, V)$. Then we can go backwards to get $U(T, V)$ and the equation of state. Consider

$$\left. \frac{\partial S}{\partial U} \right|_V = \frac{1}{T}. \text{ The left hand side is a function of } U \text{ and } V \text{ and the right}$$

hand side is just $1/T$. This determines U as a function of T and V . If the left hand side is simple enough, you may be able to explicitly solve for $U(T, V)$.

Also

$\left. \frac{\partial S}{\partial V} \right|_U = \frac{P}{T}$. Again the left hand side is a function of U and V. This gives P as a function of U, V, and T. Using the result for U, we can replace U with U(T,V) to get P as a function of T and V, which is the equation of state. For the ideal gas, this works out nicely. Try it.

Canonical distribution:

For a system in contact with a heat reservoir at temperature T, the probability that the system will be in a specific microstate with energy U is proportional to the Boltzmann factor

$$e^{-\frac{U}{kT}}$$

This follows directly from the fundamental assumption and the definition of temperature above: The probability for the combination of the system and reservoir with total energy U_T to be in a state in which the system is in a single microstate with energy U is proportional to the number of microstates of the reservoir when it has energy $U_T - U$

$$P(U) \propto w_R(U_T - U) = e^{S_R(U_T - U)/k}$$

But for small U

$$S_R(U_T - U) \approx S_R(U_T) - U \left. \frac{\partial S_R(U)}{\partial U} \right|_{U=U_T} = S_R(U_T) - \frac{U}{T}$$

So

$$P(U) = P(0)e^{-\frac{U}{kT}}$$

Conclusion

“Some things just don’t happen.”