
Q vs. q for distinguishable vs indistinguishable systems

Derivation of Thermodynamic Properties from Q:

U, S, A, μ, P

Examples

• Partition Functions for independent and distinguishable particles

We want to generalize for distinguishable and indistinguishable particles. Let's make it easier on ourselves by considering only independent subsystems, i.e., the particles do not interact. Then the energy of the whole system, written as,

$$E_j = \sum_i \varepsilon_i + \left(\varepsilon_{\text{interaction}}\right)$$

can be simplified because the 2nd term ($\varepsilon_{\text{interaction}}$) is 0.

This allows us to say:

$$\underset{\text{whole system}}{Q} = \prod_i q_i$$

1. Distinguishable particles (and independent)

A, B independent of each other, and labeled:

Ⓐ Ⓑ

ε_i^A ε_m^B

i=1,2,…a m=1,2,…b

$$E_j = \varepsilon_i^A + \varepsilon_m^B$$

$$q_A = \sum_{i=1}^{a} \exp{}^{-\varepsilon_i^A}\!\big/_{kT} \quad \text{and} \quad q_B = \sum_{m=1}^{b} \exp{}^{-\varepsilon_m^B}\!\big/_{kT}$$

$$Q = \sum_{j=1}^{t} \exp{}^{-E_j}\!\big/_{kT} = \sum_{i=1}^{a}\sum_{m=1}^{b} \exp{}^{-\left(\varepsilon_i^A + \varepsilon_m^B\right)}\!\big/_{kT} = \sum_{i=1}^{a}\sum_{m=1}^{b} \exp{}^{-\varepsilon_i^A}\!\big/_{kT} \exp{}^{-\varepsilon_m^B}\!\big/_{kT}$$

Because the sums are independent of each other

$$Q = \sum_{i=1}^{a} \exp{}^{-\varepsilon_i^A}\!\big/_{kT} \sum_{m=1}^{b} \exp{}^{-\varepsilon_m^B}\!\big/_{kT} = q_A q_B$$

Generalize for N independent and distinguishable particles:

$$\boxed{Q = q^N}$$

2. Indistinguishable particles (and independent)

Now: no A and B labels!

$E_j = \varepsilon_i^A + \varepsilon_m^B$ where i=1,2,…t_1, m = 1,2,…t_2.

$$Q = \sum_{j=1}^{t} \exp{-E}\Big/_{kT} = \sum_{i=1}^{t_1}\sum_{m=1}^{t_2} \exp{-\left(\varepsilon_i^A + \varepsilon_m^B\right)}\Big/_{kT}$$

Now: cannot factor out of sum due to indistinguishability: can't separate sums

WHY?

particle 1 ε_1=10

particle 2 ε_1=167

Can't be distinguished from the situation where

particle 1 ε_1=167

particle 2 ε_1=10

So overcounting is present. Divide by 2!

$$Q = \frac{q^2}{2!}$$

In general, for N particles, divide by N!

$$\boxed{Q = \frac{q^N}{N!}}$$

- ## Deriving Thermodynamic Properties using Q

All thermodynamic quantities can be calculated from the partition function

The Boltzmann factor and partition function are the two most important quantities for making statistical mechanical calculations. ***If we have a model for a material for which we can calculate the partition function, we know everything there is to know about the thermodynamics of that model***.

Now we will relate our favorite thermodynamic properties to q, the partition function. This is our link between the microscopic and macroscopic descriptions. Using the convenient dummy variable β = $1/k_bT$ to simplify things.

Deriving Energy, U

$$\langle E \rangle = \sum_{j=1}^{t} p_j E_j$$

$$= \frac{1}{Q} \sum_{j=1}^{t} E_j e^{-\beta E_j}$$

Use trick

$$\left(\frac{\partial Q}{\partial \beta} \right) = \frac{\partial}{\partial \beta} \sum e^{-\beta E_j} = -\sum E_j e^{-\beta E_j}$$

so then

$$\langle E \rangle = \frac{1}{Q} \sum_{j=1}^{t} E_j e^{-\beta E_j}$$

$$= -\frac{1}{Q} \left(\frac{\partial Q}{\partial \beta} \right) = -\left(\frac{\partial \ln Q}{\partial \beta} \right)$$

Substituting this into <E>

$$U = < E > = -\left(\frac{\partial \ln Q}{\partial T} \right) \left(\frac{\partial T}{\partial \beta} \right)$$

$$\left(\frac{\partial \beta}{\partial T} \right) = \frac{\partial}{\partial T} \left(\frac{1}{kT} \right) = -\frac{1}{kT^2}$$

$$\boxed{U = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)}$$

Deriving S:

$$\frac{S}{k} = -\sum_{j}^{t} p_j \ln p_j$$

Use

$$p_j = \frac{e^{-E_j / kT}}{Q}$$

$$\frac{S}{k}=-\sum_j^t\left(\frac{1}{Q}e^{-E_j/kT}\right)\left(\ln\left(\frac{1}{Q}\right)-\frac{E_j}{kT}\right)$$

Split Σ up

$$\frac{S}{k}=-\sum_j^t\left(\frac{1}{Q}e^{-E_j/kT}\right)\ln\left(\frac{1}{Q}\right)+\sum_j^t\frac{1}{Q}e^{-E_j/kT}\left(\frac{E_j}{kT}\right)$$

1st term:

$$-\sum_j^t\frac{1}{Q}e^{-E_j/kT}\ln\frac{1}{Q}$$

$$=+\frac{1}{Q}\sum_j^t e^{-E_j/kT}\ln Q$$

$$=\frac{1}{Q}\cdot Q\cdot\ln Q$$

$$=\ln Q$$

2nd term:

$$\sum_j^t\frac{1}{Q}e^{-E_j/kT}\left(\frac{E_j}{kT}\right)=\frac{1}{Q}\cdot\frac{1}{kT}\sum_j^t E_j e^{-E_j/kT}$$

Use

$$U=\frac{1}{Q}\sum_j^t E_j e^{-E_j/kT}$$

So 2nd term is

$$\sum_j^t\frac{1}{Q}e^{-E_j/kT}\left(\frac{E_j}{kT}\right)=\frac{1}{Q}\cdot\frac{1}{kT}\sum_j^t E_j e^{-E_j/kT}=\frac{U}{kT}$$

Combing both terms:

$$\boxed{S=k\ln Q+\frac{U}{T}}$$

We can do this for several other properties!

Helmholtz Free Energy, A

$$A=U-TS$$

$$=U-T\left(k\ln Q+\frac{U}{T}\right)$$

$$=-kT\ln Q$$

Chemical potential, μ

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

$$\mu = -kT\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V}$$

Pressure, P

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$$

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}$$

Now have all the thermodynamic properties as a function of Q, the partition function. We can use these in a couple examples.

• An Application Example: Visualizing the complex states of a DNA molecule

Let's consider the unwinding of a superhelix of DNA as an example of using the Gibbs free energy to describe the population of states.

Closed superhelical DNA can be 'unwound' by treatment with DNAse, which 'nicks' the DNA. The break in one chain allows the double helix to twist relative to its axis and relax the supercoiling in response to thermal fluctuations. The DNA can be 'healed' by treatment with ligase to seal the nick. When nicked, the DNA will achieve an equilibrium where some of the DNA is completely unwound, some has one right-handed twist, some has one left-handed twist, some has two right-handed twists, and so on. When the ligase is added to 'freeze' the fluctuating DNA by fixing the nick, the collection of DNA molecules is captured in an equilibrium distribution of different configurations. We can use the connection between the probability of configurations and the free energy to predict this distribution. (Eisenberg and Crothers)

The 'frozen' collection of DNA molecules with different degrees of superhelicity can be separated by gel electrophoresis to allow analysis of the relative concentrations of each species:

The gel electrophoresis chart shows a clear separation of unique DNA species, occurring at different concentrations as a function of their superhelicity. (The y-axis represents concentration, while the x-axis represents distance along the gel.) The peaks have been denoted with values of e, measuring the number of superhelical twists in the DNA present in each peak: ε = relaxed circular DNA, ε+1 =

one left-handed superhelical twist, ε-1 = one right-handed superhelical twist, etc.

How can we predict the relative concentrations observed above? As with all statistical mechanics calculations, we start with a model: Here, we want a model for how the free energy varies with twist in the DNA superhelix.

We will start from a very simple model for the twisting energy of the DNA coil (…and show that it correctly predicts the observed distribution of twists). We are all familiar with the simple linear function known as Hooke's law which describes the relationship between the restoring force on a spring and the displacement of the spring: F = -kx, where k is the spring constant. Twisting DNA is not a simple spring, but can be thought of as a torsional spring- a coil with a restoring force when a torque is applied. To remind you, a torque (T) results when a force acts in a radial manner through an axis r:

$$\mathrm{T} = \overline{F} \times \overline{r}$$

Both the force $\overline{F}$ and radius $\overline{r}$ are vectors. Analogous to the simple linear spring, a torsional spring feels a torque which is linear to the applied twist:

$$\mathrm{T}_{torsional\_spring} = -k_T \theta$$

Here k_T is a torsional spring constant and θ is the angle of the twist. If we assume the spring can only undergo integral numbers of twists, then we could rewrite this as:

$$\mathrm{T}_{torsional\_spring} = -k_T \theta_{twist} \tau$$

Where θ_{twist} is simply the angle for one twist of the spring, and τ is the total number of twists ($\theta = \theta_{twist}\tau$). Just as the force on a linear spring is related to a change in potential energy $F = -kx = -\frac{\partial V}{\partial x}$, we can relate the torque on our DNA torsional spring to a change in its free energy:

$$\mathrm{T}_{torsional\_spring} = -k_T \theta_{twist} \tau = -\frac{\partial G}{\partial \tau}$$

$$\therefore \frac{\partial G}{\partial \tau} = k_T \theta_{twist} \tau = B\tau$$

$$G = \frac{B}{2}\tau^2$$

In the equation above, we combine the constants into one stiffness parameter B ($B = k_T\theta_{twist}$) to simplify the expression. We are using free energy rather than mechanical potential energy here because this molecular system (the twisting DNA coil) has internal degrees of freedom (e.g., bonds among the DNA strands) that could also be affected by supercoiling.

If we ask what is the free energy of one particular DNA molecule *i* that has some number of twists τ_i, we have:

$$G_i = \frac{B\tau_i^2}{2}$$

τ is the number of superhelical turns; negative for right-hand turns, positive for left-hand turns.

Using our link between the free energy and the probability of observing a state with a particular energy we have for the twisting DNA:

$$P_i = \frac{e^{-\frac{B\tau_i^2}{2RT}}}{\sum_{n=1}^{\text{all energies}} e^{-\frac{B\tau_n^2}{2RT}}}$$

To relate this to our measured quantity (concentration of species *I*, proportional to the peak in our gel electrophoresis experiment), we simply recognize:

$$c_i = c_o P_i$$

Where $\boldsymbol{c_o}$ is the total concentration of DNA. The presence of the squared term in the exponent means this distribution has a Gaussian shape (the same result we discussed last lecture- except for this simple model, the entire probability distribution is Gaussian, not just near the peak of the distribution). Fitting the measured concentration data with a Gaussian curve, we find the theory predicts the observed distribution of superhelices very well:

Absolute Entropy

Third Law of thermodynamics

• Absolute Entropies

Absolute entropy of an ideal gas

Start with fundamental equation

$$dU = TdS - pdV$$

$$dS = \frac{dU + pdV}{T}$$

for ideal gas:

$$dU = C_V dT \text{ and } p = \frac{nRT}{V}$$

$$dS = \frac{C_V dT}{T} + \frac{nR}{V} dV$$

At constant T, dT=0

$$dS_T = \frac{pdV}{T}$$

For an ideal gas, pV = nRT

$$dS_T = \frac{nRdV}{V}$$

At constant T

$$d(pV) = d(nRT) = 0$$

$$pdV = -Vdp$$

plugging into dS_T:

$$dS_T = -\frac{nRdp}{p}$$

This allows us to know how S(p) if T held constant. Integrate!

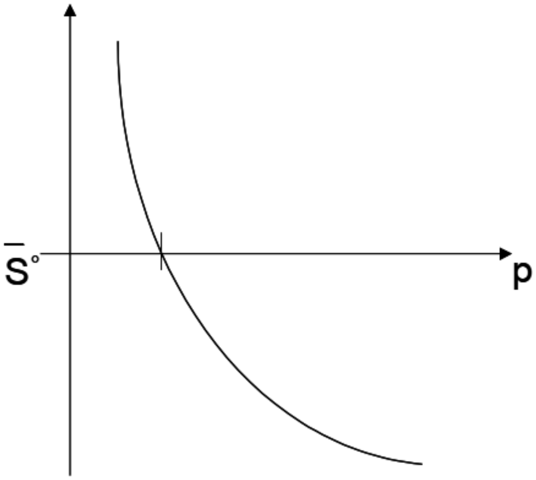
For an arbitrary pressure p,

$$S(p,T) = S(p^o,T) - \int_{p^o}^{p} \frac{nRdp}{p} = S(p^o,T) - nR\ln\left(\frac{p}{p^o}\right)$$

where p^o is some reference pressure which we set at 1 bar.

$\Rightarrow$ $S(p,T) = S^o(T) - nR \ln p$ (p in bar)

$$\boxed{\overline{S}(p,T) = \overline{S}^0(T) - R\ln p}$$



S ↓ as P↑

But to finish, we still need $\overline{S}^o(T)$!

Suppose we had $\overline{S}^o(0K)$ (standard molar entropy at 0 Kelvin)

$$dH = TdS + Vdp$$

$$dH = C_p dT$$

for ideal gas

$$C_p dT = TdS + Vdp$$

$$dS = \frac{C_p}{T}dT - \frac{V}{T}dp$$

Then using $\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$

we should be able to get $\overline{S}^o(T)$. Integrating over dS eqn, assuming C_p constant over T range:

$$dS = \int_{T_1}^{T_2} \frac{C_p}{T} dT - \int_{p_1}^{p_2} \frac{nR}{p} dp$$

So then

$$\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right) - nR\ln\left(\frac{p_2}{p_1}\right)$$

$$= C_p \ln\left(\frac{T_2}{T_1}\right) - nR\ln p \qquad \text{for } p = 1\text{bar}$$

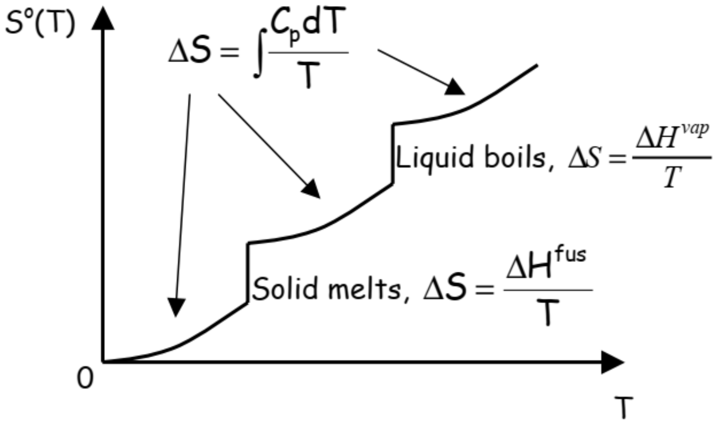
Given C_p, T_1, p_1, → T_2, p_2, can calculate ΔS.

We will use T=0K as a reference point.

Consider the following sequence of processes for the substance A:

$A(s,0K,1bar) = A(s,T_m,1bar) = A(l,T_m,1bar) = A(l,T_b,1bar) = A(g,T_b,1bar) = A(g,T,1bar)$

$$\overline{S}(T,1bar) = \overline{S}^o(0K) + \int_0^{T_m} \frac{\overline{C}_p(s)dT}{T} + \frac{\Delta\overline{H}_{fus}}{T_m} + \int_{T_m}^{T_b} \frac{\overline{C}_p(\ell)dT}{T} + \frac{\Delta\overline{H}_{vap}}{T_b} + \int_{T_b}^{T} \frac{\overline{C}_p(g)dT}{T}$$



Since ΔS^0 is *positive* for each of these processes, the entropy must have its smallest possible value at 0 K. If we take $\overline{S}°(0K)$ = zero for every pure substance in its crystalline solid state, then we could calculate the entropy at any other temperature.

This leads us to the Third Law of Thermodynamics:

• THIRD LAW:

First expressed as **Nernst's Heat Theorem**:

Nernst (1905):

> As $T \to 0$ K , $\Delta S \to 0$ for all isothermal processes in condensed phases

More general and useful formulation by **M. Planck**:

Planck (1911):

> As $T \to 0$ K , $S \to 0$ for every chemically homogeneous substance in a perfect crystalline state

Justification:

① It works!

② Statistical mechanics (5.62) allows us to calculate the entropy and indeed predicts $\overline{S}°(0K) = 0$.

This leads to the following interesting corollary:

> It is impossible to decrease the temperature of any system to T = 0 K in a finite number of steps.

How can we rationalize this statement?

Recall the fundamental equation, $dU = T\,dS - p\,dV$

$dU = C_v\,dT$ For 1 mole of ideal gas, $P = RT/V$

so $C_v\,dT = T\,dS - (RT/V)\,dV$

$$dS = C_v\,d(\ln T) + R\,d(\ln V)$$

For a spontaneous adiabatic process which takes the system from T_1 to a lower temperature T_2,

$$\Delta S = C_v \ln (T_2/T_1) + R \ln (V_2/V_1) \geq 0$$

but if $T_2 = 0$, $C_v \ln (T_2/T_1)$ equals minus infinity !

Therefore $R \ln (V_2/V_1)$ must be greater than plus infinity, which is impossible. Therefore no actual process can get you to $T_2 = 0$ K.

But you can get *very very* close!

In W. Ketterle's experiments on "Bose Einstein Condensates" (recent MIT Nobel Prize in Physics), atoms are cooled to nanoKelvin temperatures ($T = 10^{-9}$ K) … but not to 0 K !

Some *apparent* violations of the third law (but which are not !)

Any disorder at T = 0 K gives rise to S > 0

- mixed crystals

If have an unmixed crystal, N atoms in N sites:

$$\Omega = \frac{N!}{N!} = 1$$

$$S = k \ln 1 = 0$$

But if mixed crystal:

N_A of A

N_B of B

$N_A + N_B = N$

$$\Omega = \frac{N!}{N_A! N_B!}$$

$$S = k \ln \frac{N!}{N_A! N_B!}$$

Use Stirling's approx:

$$\ln N! = N\ln N - N$$

$$S = k\left(N\ln N - N - N_A\ln N_A + N_A - N_B\ln N_B + N_B\right)$$

$$= -k\left(-N\ln N + N_A\ln N_A + N_A + N_B\ln N_B\right)$$

Using mole fractions: $N_A = x_A N$, $N_B = x_B N$

$$\Delta S_{mix} = -nR\left[X_A\ln X_A + X_B\ln X_B\right] > 0 \quad \text{Always !!! Even at T=0K}$$

But a mixed crystal is <u>not</u> a pure substance, so the third law is not violated.

- Any impurity or defect in a crystal also causes S > 0 at 0 K
- Any orientational or conformational degeneracies such as in a molecular crystal causes S > 0 at 0 K, for example in a carbon monoxide crystal, two orientations are possible:

C O C O C O C O C O C O C O
C O C O C O C O C O **O C** C O
C O C O C O **O C** C O C O C O
C O C O C O C O C O C O C O