Lecture 9: 10.07.05 Free energy: applying the second law in laboratory conditions

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Today:

Reading: Engel and Reid Ch. 6.1, 6.2, (6.3 less important), 6.4

Supplementary Reading: -

Last time

- Introduction of the second law:

Mechanical equilibrium

- The power of the second law is that it can be used to determine equilibrium conditions for any thermodynamic system, under arbitrary constraints – systems that can exchange heat, exchange molecules, exchange electric charge, etc.- in response to arbitrary thermodynamic driving forces: temperature, pressure, chemical potential, etc.

- Let's show a second example: how the second law also defines the conditions for mechanical equilibrium:

  - Consider two different ideal gases **A** and **B** enclosed in a cylinder, partitioned by a movable (frictionless) piston as illustrated in the figure below. The volume of the cylinder cannot change ($V_A + V_B = constant$) but the partition can slide left or right- compressing one gas (placing it under higher pressure) while expanding the other (reducing the pressure). The gases cannot exchange heat or work with their surroundings. What will the pressure on the two gases be at equilibrium?

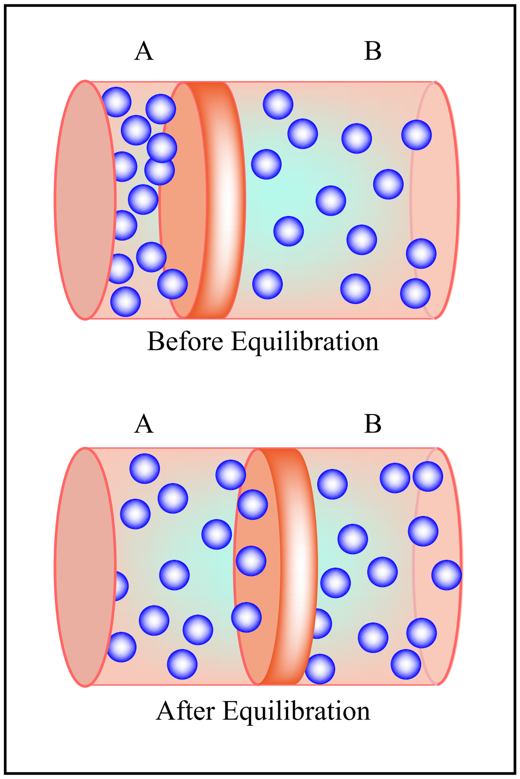


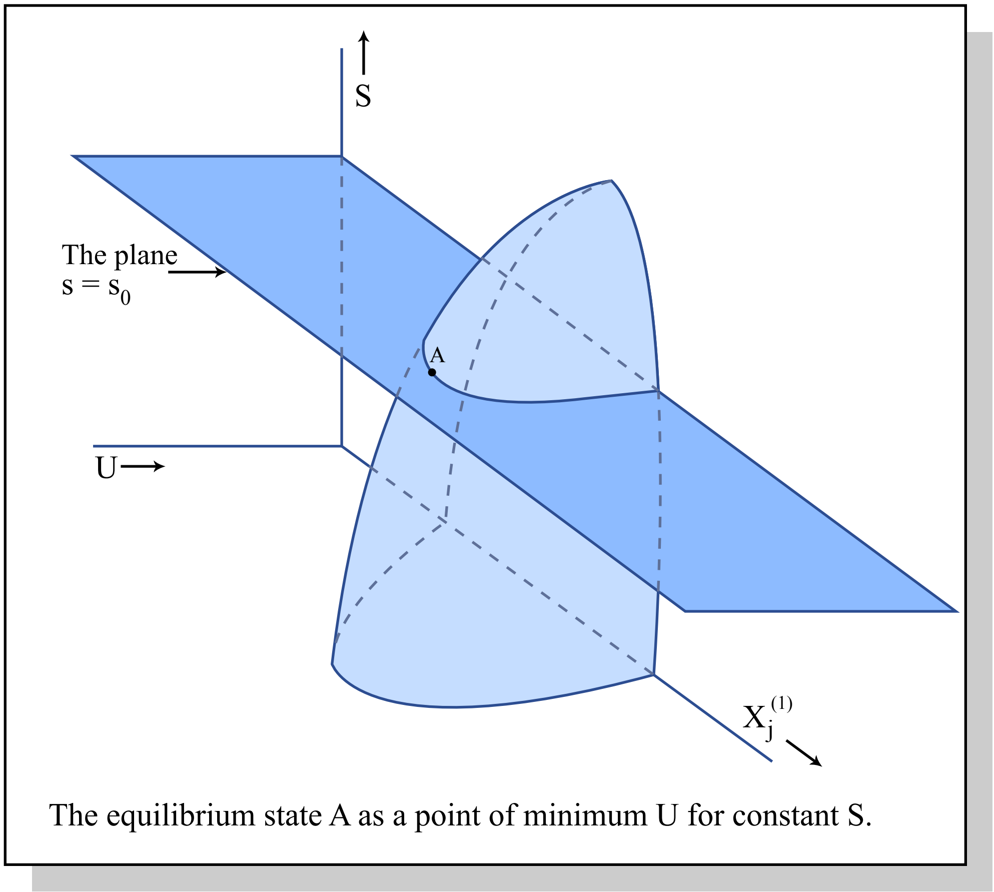
Figure by MIT OCW.

- Applying the fundamental equation for the entropy of the two gases:

    - ***Since $T_A = T_B$, this means that at equilibrium $P_A = P_B$.*** Mechanical equilibrium is reached when the pressures on the two gases are equal.

The internal energy at equilibrium

- The principle of **maximizing entropy** at equilibrium can be shown to be equivalent to **minimizing the internal energy with the entropy of the system held constant**. Graphically:



The equilibrium state A as a point of minimum U for constant S.

Figure by MIT OCW.

- Minimization of internal energy at constant total entropy is a mathematical consequence of the relationship between internal energy and entropy. We won't go through the proof here, but you can read through a short proof of it in the supplementary reading from Callen.
  - Because the absolute temperature T is always positive, and $\left(\frac{\partial U}{\partial S}\right)_{V,N} = T$, the variational statement of the second law translates to a variational statement for the internal energy at equilibrium:
  - The internal energy reaches a ***minimum*** at equilibrium.

Two new thermodynamic functions useful for laboratory conditions

Why we need another thermodynamic function

- In the calculations of equilibrium temperature and pressure we made using the second law in the last lecture, we considered **isolated systems** where transfer of heat, work, or molecules at the boundaries of the system were not allowed. (In our block A/block B heat transfer experiment, the blocks did no work and were not allowed to exchange heat with their surroundings- only with one another). In such constant internal energy systems, it is straightforward to directly apply the fundamental equation for the entropy and the second law to calculate equilibrium properties of the system.

- Though the experiments described in those calculations are physically possible, controlling heat and work flow at the boundaries of a real system is often not a simple task- and is unnecessary for most experimental procedures you would be interested in performing. Instead, what we would like to control at the boundaries of our system are the temperature and pressure (imagine a solution of a material in a test tube, as illustrated below). This is experimentally straightforward- we can place our test tube in a heating or cooling bath to maintain a constant temperature, and if the system is open to the atmosphere, it is maintained at a constant pressure (1 atm). Alternatively, if we seal the test tube with an inflexible barrier, the contents of the tube may be held at constant temperature and (approximately) volume.

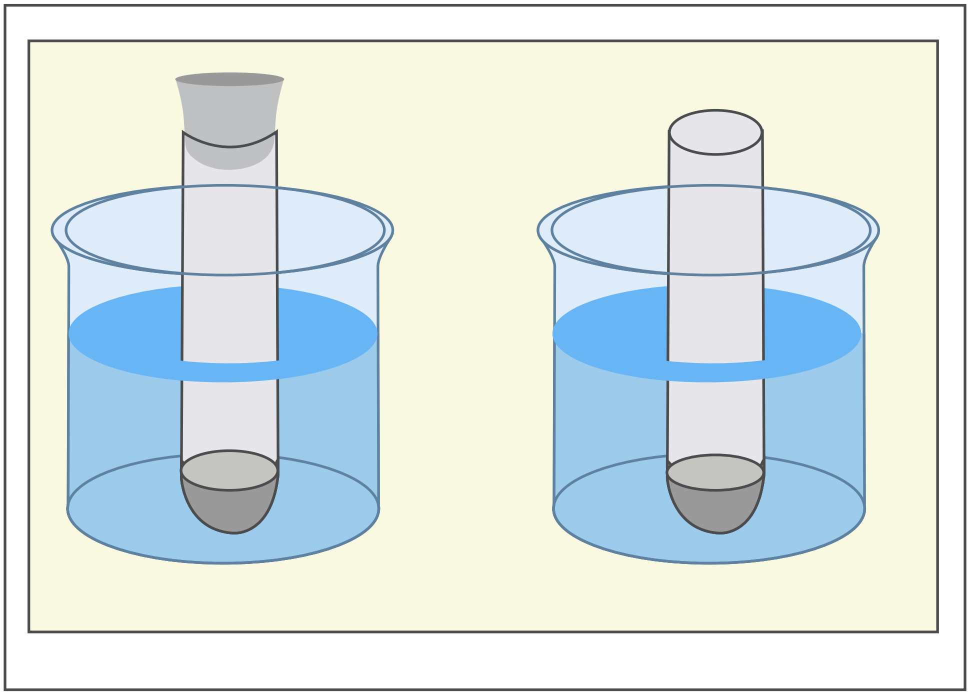
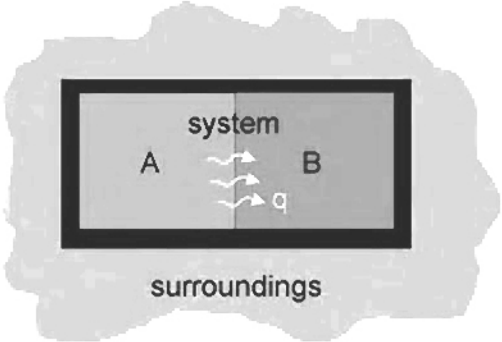


Figure by MIT OCW.

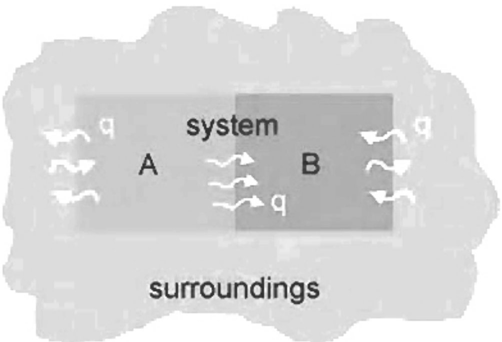
- Thus, instead of keeping the internal energy of the system constant, we would like to keep the temperature and pressure or temperature and volume constant, and predict how the system changes when various thermodynamic driving forces are applied (for our test tube example, perhaps we want to carry out a reaction on the material in the solution). We have two new complications here:
  - If we have our test tube in a heating bath, internal energy in the form of heat is being transferred into and out of the system to maintain a constant temperature, and *we can no longer apply the fundamental equation for the entropy to the system alone to determine the equilibrium state*.
  - The second law only dictates the behavior of the total entropy of the universe. Ack!

Isolated system



$\Delta S_{universe} = \Delta S_{system}$

closed system



$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$

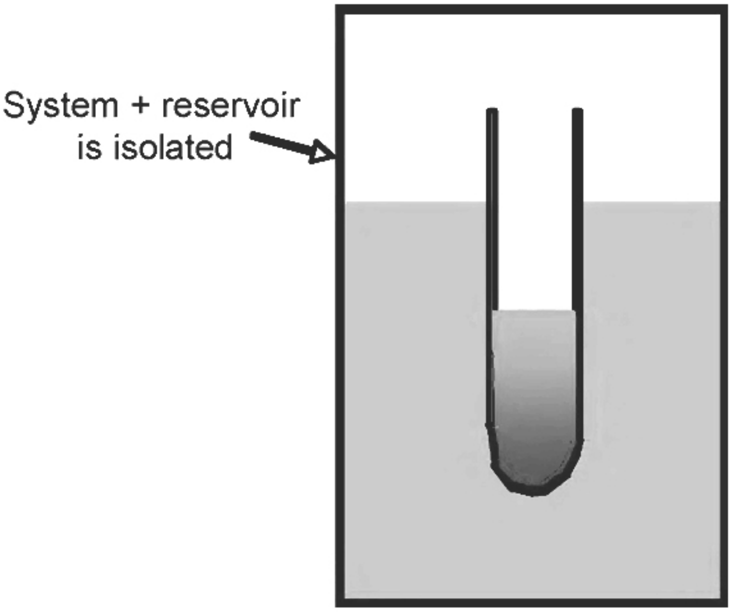
???

- **So how do we get around this problem?** *We'd much rather make calculations for the system alone*, rather than having to understand the thermodynamic behavior of the system *and* its surroundings. The solution is to define a fundamental equation designed for the conditions at hand.
- **Mathematically, it is most straightforward to make equilibrium calculations using a thermodynamic function whose independent variables are the variables controlled at the boundaries of the system**.

Equilibrium at constant temperature and pressure: Gibbs Free Energy[3]

Determining equilibrium for experiments in the lab

- The second law defines equilibrium by the change in entropy of the entire universe. As already discussed, that's an incredible pain when we are only really interested in what's happening in our test tube! The solution: let's define a new state function that will allow us to apply the second law by looking only at the changes occurring in the system. We start by imagining the real system + surroundings enclosed in an isolating box:



- The second law defines possible processes by:

$$dS_{universe} = dS_{system} + dS_{surroundings} \geq 0 \qquad \textbf{for all possible processes}$$

- We make use of the isolated nature of the system + surroundings to write constraint equations:

- Now, from the fundamental equation for the entropy, we have:

- These last two equations are, for practical calculations, perhaps the most important in thermodynamics for materials science and engineering.
    - ***In words, the second law demands that the Gibbs free energy must be lowered by the change happening to a system for that change to happen spontaneously at constant temperature and pressure. It also dictates that the Gibbs free energy at constant temperature and pressure is a minimum at equilibrium.***

What's 'free' in the Gibbs free energy?

- We defined a useful thermodynamic function (the enthalpy, *H*) by simply subtracting the 'mechanical' component of the internal energy from *U*. In a similar manner, Gibbs free energy (G) is defined by subtracting both the 'thermal' energy and the 'compressive' energy from U:

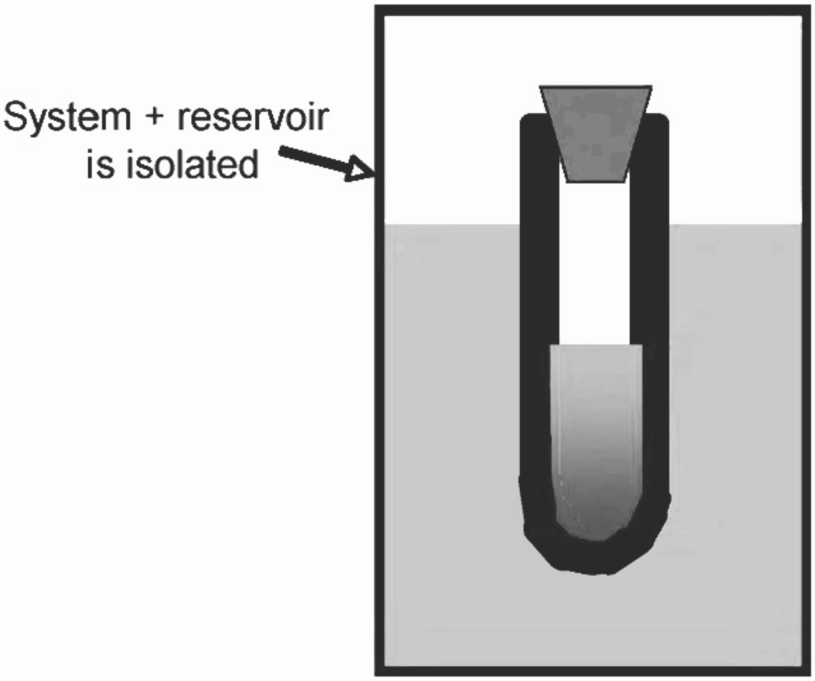
- But what *is* the Gibbs free energy? We've taken the total internal energy and subtracted off the thermal energy and the compressive energy- what's left? The answer: energy arising from other kinds of work terms. So far we've mostly focused on two sources of internal energy, compressive work from an applied pressure and thermal energy due to heat transfer. However, we also introduced other types of work: work of polarization, chemical work, magnetic work, etc.
    - *In many practical problems in materials science & engineering, it is these other kinds of work in which we are most interested…*

- The differential form of the Gibbs free energy (***the fundamental equation for the free energy***) is useful for many calculations in multicomponent/multiphase systems:

Equilibrium at constant temperature and volume: Helmholtz Free Energy[1]

- A second common 'real-world' situation is the case of a system equilibrated at constant temperature and held at constant volume. Though this is often difficult to realize experimentally, it is especially important for many theoretical calculations, and particularly computer simulations, where constant volumes are easy to model. (We will make extensive use of this situation in statistical mechanics later in the term). Again, to facilitate predictions of spontaneous processes under conditions of constant temperature and constant volume, we'd like a thermodynamic function *for the system* that satisfies the second law by being maximized or minimized at equilibrium.

- Imagine for concreteness that we have a test tube in a heat bath as depicted in the left-hand figure above. The bath and test tube are isolated from their surroundings and do not exchange heat, work, or atoms with the atmosphere/benchtop/etc. The test tube is the system of interest, but because the tube is exchanging heat with the bath, we must also consider the entropy of the heat bath (the surroundings). Together, the heat bath + test tube *do* form an isolated system, so the fundamental equation for the entropy can be used to apply the second law to the pair (nothing else in the universe is being affected by the test tube and bath):



$$dS_{universe} = dS_{surr} + dS_{system} \geq 0$$ second law for the tube + heat bath

$$dS_{surr} = \frac{dU_{surr}}{T} + \frac{P}{T}dV_{surr} = -\frac{dU_{system}}{T_{system}}$$

$$dS_{universe} = -\frac{dU_{system}}{T_{system}} + dS_{system} \geq 0$$

$$\frac{dU_{system}}{T_{system}} - dS_{system} \leq 0 \Rightarrow dU_{system} - TdS_{system} \leq 0$$

  - These equations give us a thermodynamic function that is minimized to satisfy the second law for a system held at constant temperature and pressure. ***With this equation we do not need to know the state of the heat bath***- we only need to know the state of the system itself.

- The differential above is defined as a new thermodynamic function: The Helmholtz free energy:

- As an aside, the derivation of the Helmholtz and Gibbs free energies is an example of a change of variables- changing from maximizing entropy of a system at constant *(U,V,N)* to minimizing free energy of a system at constant *(T, V, N)*. There are multiple ways to arrive at this change of variables, known as a **Legendre transformation**.

Mathematical Theorems to Extend our Calculations

The Euler Relationship and Maxwell Relations

- We've already discussed some of the useful properties of state functions like U, S, and H- they are path independent and integrable. An additional useful characteristic is that state functions must obey the Euler reciprocal relationship, which is expressed mathematically for a multivariable function f*(x,y)* as:

(Eqn 9)

$$\frac{\partial^2 f(x,y)}{\partial x \partial y} = \frac{\partial^2 f(x,y)}{\partial y \partial x}$$

EULER RELATIONSHIP

  - The Euler relationship can be used to identify identities between thermodynamic variables that are not obvious; these are called the *Maxwell relations*.

- A set of Maxwell relations can be derived for each thermodynamic state function. For example, starting with the internal energy *U(S,V,N)*:

    - Maxwell's relations can help us further derive thermodynamic quantities from measurable parameters of our materials.

- Another example is the Maxwell relation obtained by taking second derivatives of the enthalpy *H(S,P,N):*

- We have two more key thermodynamic functions we will use this term, which also have Maxwell relations:
  - Gibbs free energy:
    - $G = H - TS$
    - Maxwell relation: $-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$
  - Helmholtz free energy:
    - $F = U - TS$

- Maxwell relation: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

U	$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S$
$H \equiv U + PV$	$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S$
$G \equiv H - TS$	$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$
$F \equiv U - TS$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

References

1. Dill, K. & Bromberg, S. Molecular Driving Forces (New York, 2003).
2. Callen, H. B. Thermodynamics (Wiley & Sons, New York, 1960).
3. Carter, W. C. (2002).