Lecture 17

Conditions of Equilibrium

Last Time

The behavior of $\Delta\overline{G}$ near equilibrium

Survey Molar Entropies

Extrapolation to Unstable States

Microscopic Origins of Entropy

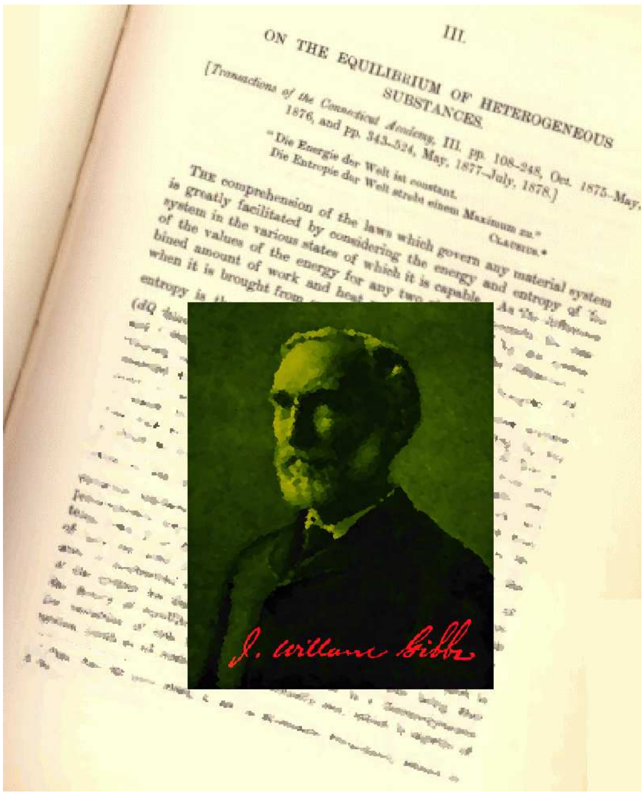
Equilibrium Thermodynamics

The foundations of thermodynamics were developed in an era where steam engines and production of useful work were the most important issues. Joule was interested in motors and the original statement of the second law derives from Carnot who was trying to find limits on the efficiency of work cycles. I've avoided this approach of engines and cycles in these lectures because, today, the most interesting applications of thermodynamics apply to the equilibrium and near-equilibrium properties of material systems.

A short list of practical applications for which thermodynamics is the essential tool for understanding includes:

1. Is it possible to make such-and-such a material and, if so, what processing variables make it possible?
2. If I have so-and-so material and I put it in service in a particular environment, will it remain that way?
3. What are the limiting properties of such a material? What is the maximum response?
4. What processes make a material unstable?
5. How do I formulate a prediction for how a material will change in time (kinetics)?

Our current understanding of equilibrium, derived from the second law of thermodynamics, derives from a remarkably accomplished paper written by Gibbs at the beginning of the twentieth century. We will begin by abstracting the first 10 pages of that 300-page paper.



III.

ON THE EQUILIBRIUM OF HETEROGENEOUS SUBSTANCES.

[Transactions of the Connecticut Academy, III. pp. 108–248, Oct. 1875–May, 1876, and pp. 343–524, May, 1877–July, 1878.]

"Die Energie der Welt ist constant.
Die Entropie der Welt strebt einem Maximum zu."
CLAUSIUS.

Figure 17-1: J. Willard Gibbs 1839-1903 , The Architect of Modern Equilibrium Thermodynamics.

Unconstrained Equilibrium

Consider a an isolated system, in this case:
$dU = 0$ and $dV = 0$

If we consider a system that can only perform PV-work on its surroundings, we can write for any quasi-static (constantly in equilibrium).

$$dS = \frac{dU}{T} + \frac{PdV}{T} \tag{17-1}$$

Therefore, at equilibrium the entropy must be a maximum or a minimum ($dS = 0$) (This is the equation of a tangent plane)

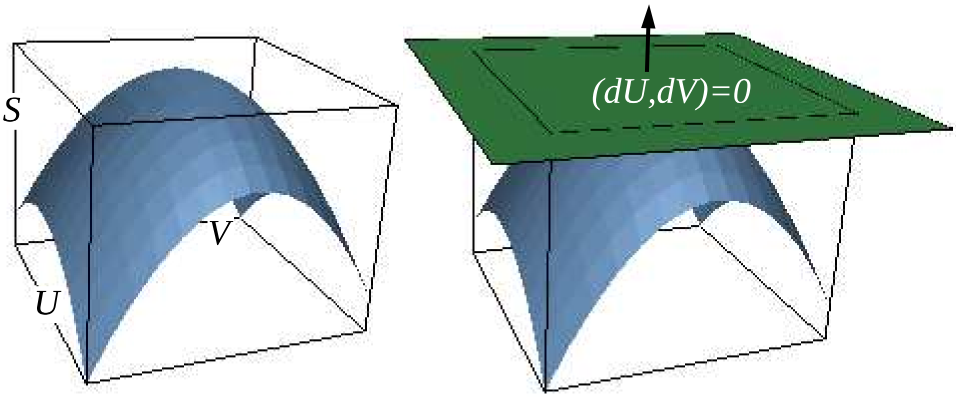


Figure 17-2: The surface of S as a function of U and V

Since entropy must always increase as a system approaches equilibrium, it must be a maximum at equilibrium. (In other words, it must be at the summit of a hill with U given as north and V given as west.)

How to express this maximal relationship?

Let δS represent any possible variation (change internal temperature, distribution, heat flow, etc.) to the entropy. Then, if the supposed variation also has $\delta U = \delta V = 0$,

$$(\delta S)_{\delta U = 0\,,\,\delta V = 0} \leq 0 \tag{17-2}$$

implies S is a maximum and is thus the equilibrium state.

This introduces the concept of a *virtual* change:

Equation 17-2 is equivalent to

$$(\delta U)_{\delta S=0\,,\,\delta V=0} \geq 0 \tag{17-3}$$

(See if you can figure out why—hint: $(\partial U/\partial S)_V = T > 0$
Implies U is a minimum at constant S and V—and that is what we expect from mechanics.

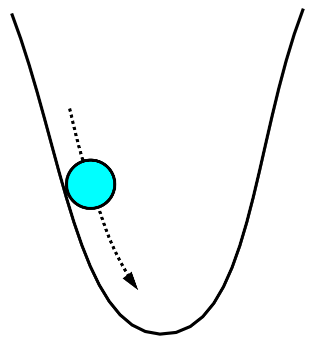


Figure 17-3: Ball rolling on a surface.

Implications

Consider an isolated system with two separate regions at uniform (but potentially different) pressures and temperatures.

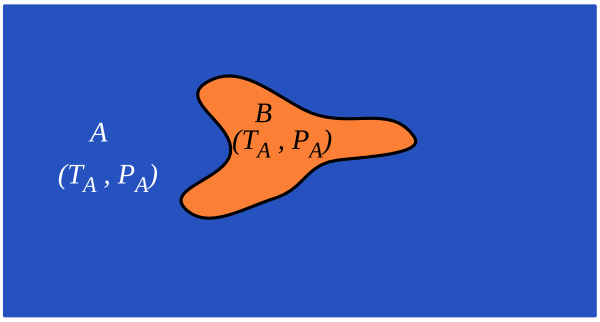


Figure 17-4: Region A with pressure and temperature P_A and T_A enclosing a subregion B at P_B and T_B.

Suppose that there is a "virtual" change (i.e. any one of an infinite number of possible changes) in the system such that $\delta U = 0$ and $\delta V = 0$.

Any change in B (δU_B, δV_B) can be chosen as a virtual changes as long as we also pick for system A, ($\delta U_A = -\delta U_B$ and $\delta V_A = -\delta V_B$).

Then

$$\begin{aligned}\delta S^{\text{total}} &= \delta S_A + \delta S_B \\ &= \frac{1}{T_A}(\delta U_A + P_A \delta V_A) + \frac{1}{T_B}(\delta U_B + P_B \delta V_B) \\ &= \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\delta U_A + \left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right)\delta V_A\end{aligned} \tag{17-4}$$

Because δU_A is independent of δV_B we can find a $\delta S_{total} > 0$ unless

$$\left(\frac{1}{T_A} - \frac{1}{T_B}\right) = 0 \quad \Longrightarrow \quad T_A = T_B \tag{17-5}$$

$$\left(\frac{P_A}{T_A} - \frac{P_B}{T_B}\right) = 0 \quad \Longrightarrow \quad P_A = P_B \tag{17-6}$$

These are the necessary conditions for equilibrium in a heterogeneous isolated system: no spatial variation pressure can exist if the volume can move from region to region (δV) and no spatial variation in temperature can exist if energy can flow from region to region (δU).[18]

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[18] Any energy associated with a change in size of the interface has been neglected; this extra energy, which derives from the surface tension, will be important later and will alter the condition that the pressures are equal.