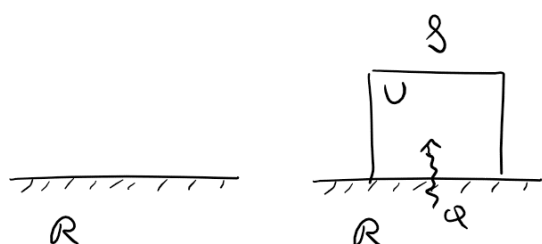


Lecture 9 – Thermodynamic potentials

LAST TIME: In Lect. 7 we introduced the Helmholtz free energy $F = U - TS$ when discussing the canonical ensemble.

F is minimized at equilibrium for a system \mathfrak{S} of fixed volume V maintained at constant T by a reservoir \mathcal{R} .

TODAY: U and F are examples of thermodynamic potentials



What does F really represent?

Let's say we could create a system \mathfrak{S} from nothing, in an environment at constant T . How much work does this cost us?

We have to provide energy $U_{\mathfrak{S}}$ of system, but \mathfrak{S} can extract heat $Q = T\Delta S$ from reservoir \mathcal{R} for free.

As long as $\Delta S_{\mathcal{R}+\mathfrak{S}} \geq 0$, we can transfer Q from \mathcal{R} to \mathfrak{S} without violating 2nd law.

So, actual cost to us is:

$$U_{\mathfrak{S}} - TS_{\mathfrak{S}} = F_{\mathfrak{S}}$$

($S_{\mathfrak{S}} = \Delta S_{\mathfrak{S}}$ is the total entropy of system \mathfrak{S} .)

F = work provided to create \mathfrak{S} at constant T

(Conversely, F = work we can extract to annihilate \mathfrak{S} . We cannot take the entropy S because then \mathcal{R} would be left with less, violating the second law).

To see this explicitly, look at the change in F at constant T :

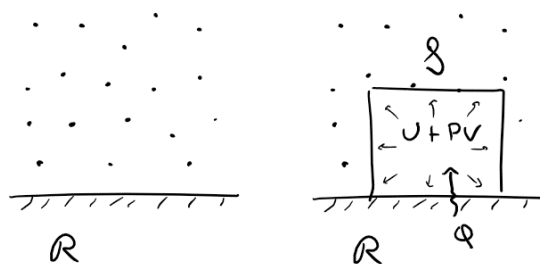
$$\Delta F = \Delta U - T\Delta S = \cancel{Q} + W - \cancel{T\Delta S} \quad \text{so} \quad W = \Delta F$$

$Q + W$

True for a reversible process. If there is irreversibility recall $T\Delta S > Q$, so

$$W \geq \Delta F \text{ at constant } T, V$$

(This is an alternate way of writing the 2nd law.)



KEY CONCEPT: Enthalpy and Gibbs free energy

Now consider a system \mathcal{S} in an atmosphere, i.e. an environment or reservoir \mathcal{R} that maintains a constant pressure p and temperature T (e.g. this classroom at $p = 1$ atm)

Now in the work required to create \mathcal{S} from nothing, we need to provide not only the energy $U_{\mathcal{S}}$ of the system, but also displace a volume V of atmosphere at pressure p around \mathcal{S} , which costs $+pV_{\mathcal{S}}$. This sum is called the enthalpy:

$$H_{\mathcal{S}} \equiv U_{\mathcal{S}} + pV_{\mathcal{S}}$$

Once again, we subtract the heat we can extract from \mathcal{R} for free to get the work required to create \mathcal{S} :

$$G_{\mathcal{S}} \equiv U_{\mathcal{S}} + pV_{\mathcal{S}} - TS_{\mathcal{S}}$$

which is called the Gibbs free energy.

(Conversely, G = work we can extract to annihilate \mathcal{S} at constant p . We cannot take the entropy S because then \mathcal{R} would be left with less, and the atmosphere automatically does work $-pV$ in collapsing into the vacuum left by \mathcal{S} .)

Explicitly, consider a change in G at constant p :

$$\begin{aligned} \Delta G &= \Delta U + p\Delta V - T\Delta S = \cancel{Q} + W + p\Delta V - \cancel{T\Delta S} \\ &= Q + W \\ &= W + p\Delta V \end{aligned}$$

Define the effective work W' , i.e. work other than that done automatically by the atmosphere:

$$W' \equiv W - (-p\Delta V)$$

Like before:

$$W' \geq \Delta G \text{ at constant } p, T$$

Note: what is the difference between Helmholtz and Gibbs free energies?

F is useful in situations where T, V are maintained constant (e.g. many systems in condensed matter physics). G is useful where p, T are maintained constant (e.g. many systems in chemistry & biology, such as chemical reactions, where V can change).

Also, we will see that G , similar to F , is minimized at equilibrium for a system \mathcal{S} maintained at constant T and pressure p by a reservoir \mathcal{R} .

These 4 quantities are called the thermodynamic potentials:

Energy: $U = U(S, V)$

$$dU = TdS - pdV \text{ from thermodynamic identity}$$

Helmholtz free energy: $F = F(T, V) \equiv U - TS$

↑

once T, V are fixed, you've set F

$$\begin{aligned} dF &= dU - TdS - SdT \\ &= \cancel{TdS} - pdV - \cancel{TdS} - SdT \quad \text{since } dU = TdS - pdV \\ &= -SdT - pdV \end{aligned}$$

Question 1: Find the two natural variables H and G depend on by writing out the differential equation for each

Enthalpy: $H = H(p, S) \equiv U + pV$ since

$$\begin{aligned} dH &= dU + pdV + Vdp \\ &= TdS - \cancel{pdV} + \cancel{pdV} + Vdp \quad \text{since } dU = TdS - pdV \\ &= TdS + Vdp \end{aligned}$$

Gibbs free energy: $G = G(p, T) \equiv U + pV - TS = H - TS$ since

$$\begin{aligned} dG &= dU + pdV + Vdp - TdS - SdT \\ &= \cancel{TdS} - \cancel{pdV} + \cancel{pdV} + Vdp - \cancel{TdS} - SdT \quad \text{since } dU = TdS - pdV \\ &= -SdT + Vdp \end{aligned}$$

KEY CONCEPT: Maxwell relations

Notice all 4 potentials are functions of two independent variables:

S or T, p or V (one extensive, one intensive)

In general, for a function of two variable $f(x, y)$:

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$

where $\left(\frac{\partial f}{\partial x} \right)_y$ denotes a derivative with respect to x , keeping y fixed

Also:

$$\left(\frac{\partial}{\partial x} \right)_y \left(\frac{\partial f}{\partial y} \right)_x = \frac{\partial^2 f}{\partial x \partial y} = \left(\frac{\partial}{\partial y} \right)_x \left(\frac{\partial f}{\partial x} \right)_y$$

This general property leads to useful expressions called Maxwell relations:

$$dU = TdS - pdV$$

$$= \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV \quad \text{so } T = \left(\frac{\partial U}{\partial S} \right)_V \text{ and } p = - \left(\frac{\partial U}{\partial V} \right)_S, \text{ and}$$

$$\text{Maxwell relation ①: } \left(\frac{\partial T}{\partial V} \right)_S = \frac{\partial^2 U}{\partial S \partial V} = - \left(\frac{\partial p}{\partial S} \right)_V$$

$$dF = -SdT - pdV$$

$$= \left(\frac{\partial F}{\partial T} \right)_V dT + \left(\frac{\partial F}{\partial V} \right)_T dV \quad \text{so } S = - \left(\frac{\partial F}{\partial T} \right)_V \text{ and } p = - \left(\frac{\partial F}{\partial V} \right)_T, \text{ and}$$

$$\text{Maxwell relation ②: } \left(\frac{\partial S}{\partial V} \right)_T = - \frac{\partial^2 F}{\partial T \partial V} = \left(\frac{\partial p}{\partial T} \right)_V$$

Question 2: Derive two more Maxwell relations using the next two thermodynamic potentials

$$dH = TdS + Vdp$$

$$= \left(\frac{\partial H}{\partial S} \right)_p dS + \left(\frac{\partial H}{\partial p} \right)_S dp \quad \text{so } T = \left(\frac{\partial H}{\partial S} \right)_p \text{ and } V = \left(\frac{\partial H}{\partial p} \right)_S, \text{ and}$$

$$\text{Maxwell relation ③: } \left(\frac{\partial T}{\partial p} \right)_S = \frac{\partial^2 H}{\partial p \partial S} = \left(\frac{\partial V}{\partial S} \right)_p$$

$$dG = -SdT + Vdp$$

$$= \left(\frac{\partial G}{\partial T} \right)_p dT + \left(\frac{\partial G}{\partial p} \right)_T dp \quad \text{so } S = - \left(\frac{\partial G}{\partial T} \right)_p \text{ and } V = \left(\frac{\partial G}{\partial p} \right)_T, \text{ and}$$

$$\text{Maxwell relation ④: } \left(\frac{\partial S}{\partial p} \right)_T = - \frac{\partial^2 G}{\partial p \partial T} = - \left(\frac{\partial V}{\partial T} \right)_p$$

All of these relations come about, ultimately, from $S = S(U, V)$ and the equation:

$$\begin{aligned} dS &= \frac{1}{T} dU + \frac{p}{T} dV \\ &= \left(\frac{\partial S}{\partial U} \right)_V dU + \left(\frac{\partial S}{\partial V} \right)_U dV \end{aligned}$$

That we introduced in an earlier lecture.

What are the Maxwell relations used for?

Ex: Let's say we measure T, V of a gas and want to get entropy S . Natural variable for S are U, V , but we want $S(T, V)$:

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV$$

How do we proceed?

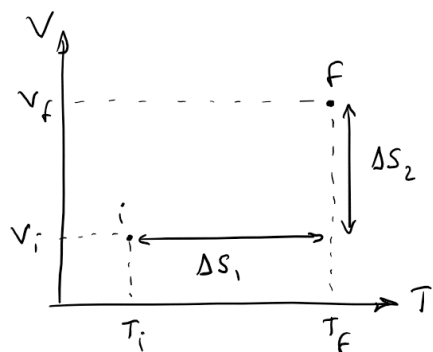
Recall heat capacity at constant volume from Lect. 6: $C_V = \left(\frac{dQ}{dT} \right)_V = T \left(\frac{\partial S}{\partial T} \right)_V$

and Maxwell relation ②: $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial p}{\partial T} \right)_V$

so,

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T} \right)_V dV$$

C_V is something that is easily measured, and so is $p(T, V)$, which is the so-called equation of state (e.g. for an ideal gas, this is the ideal gas law $pV = Nk_B T$)



From S at T_i, V_i , we can get S at T_f, V_f in two steps:

$$\text{Step 1: } \Delta S_1 = \int_{T_i}^{T_f} dT \frac{C_V(T, V_i)}{T}$$

$$\text{Step 2: } \Delta S_2 = \int_{V_i}^{V_f} dV \left(\frac{\partial p(T_f, V)}{\partial T} \right)_V$$

Since S is a function of the state only, the order of the steps do not matter.

$$S(T_f, V_f) = S(T_i, V_i) + \Delta S_1 + \Delta S_2 = S(T_i, V_i) + \int_{T_i}^{T_f} dT \frac{C_v}{T} + \int_{V_i}^{V_f} dV \left(\frac{\partial p}{\partial T} \right)_V$$

Question 3: Determine ΔS_1 and ΔS_2 defined above for a monatomic ideal gas

Hint: for a monatomic ideal gas $C_v = \frac{3}{2} Nk_B$

(Recall that $C_v = T \left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial U}{\partial T} \right)_V$ since $dU = TdS - p dV$ at constant V , and $U = \frac{3}{2} Nk_B T$)

$$\Delta S_1 = \int_{T_i}^{T_f} dT \frac{C_v}{T} = \frac{3}{2} Nk_B \int_{T_i}^{T_f} \frac{dT}{T} = \frac{3}{2} Nk_B \ln \frac{T_f}{T_i}$$

Also the equation of state is $pV = Nk_B T$, so

$$\Delta S_2 = \int_{V_i}^{V_f} dV \left(\frac{\partial p}{\partial T} \right)_V = Nk_B \int_{V_i}^{V_f} \frac{dV}{V} = Nk_B \ln \frac{V_f}{V_i}$$

Therefore

$$S(T_f, V_f) = S(T_i, V_i) + \frac{3}{2} Nk_B \ln \frac{T_f}{T_i} + Nk_B \ln \frac{V_f}{V_i}$$

This makes perfect sense since we know from the Sackur-Tetrode equation that

$$S(T, V) = Nk_B \ln(T^{3/2} V) + \text{constant terms}$$