

# Lecture 9

## Availability

At the end of the last lecture, we defined a new term called the availability,

$$dA = dU + P_0 dV - T_0 dS.$$

and deduced that for any process, changes in this term must be less than or equal to zero. That is,

$$dA \leq 0.$$

So how does that help us? Consider the following examples.

### A process at fixed entropy and volume

This means that  $dS = 0$  and  $dV = 0$ .

Thus, we have that

$$dA = dU$$

and

$$dA = dU \leq 0.$$

As such, we must minimise the internal energy  $U$  to find the equilibrium state of this system.

### Fixed entropy & pressure

This means that  $dS = 0$  and  $dP = 0$ . Thus, we have that

$$dA = dU + P_0 dV$$

Recalling now that the enthalpy  $H = U + PV$ , such that

$$dH = dU + P dV + V dP$$

which, for constant pressure, becomes

$$dH = dU + P dV$$

As such, the change in availability is given by

$$dA = dH \leq 0.$$

As such, we must minimise the enthalpy  $H$  to find the equilibrium state of this system.

## Thermally isolated & fixed volume

If a system is thermally isolated, then  $dU = 0$ . Thus

$$dA = -T_0 dS \leq 0$$

which gives

$$dS \geq 0$$

As such, we must maximise the entropy to the find equilibrium state of this system.

## Fixed temperature & volume

This means that  $dT = 0$  and  $dV = 0$ . Thus, we have that

$$dA = dU - T_0 dS$$

Recalling that the Helmholtz Free Energy is  $F = U - TS$ , and following the same steps as for the fixed entropy and pressure scenario, we are left with

$$dA = dF \leq 0.$$

So we must minimise the Helmholtz Free energy to find the equilibrium state.

## Fixed pressure and temperature

This means that  $dT = 0$  and  $dP = 0$ . Thus, we have that

$$dA = dU + P_0 dV - T_0 dS \leq 0$$

Recalling that the Gibbs Free Energy is  $G = H - TS = U + PV - TS$ , we get that

$$\begin{aligned} dG &= dU + P_0 dV + V dP_0 - T_0 dS - S dT_0 \\ &= dU + P_0 dV - T_0 dS \end{aligned}$$

for constant  $T_0$  and  $P_0$ . We then get

$$dA = dG \leq 0$$

So we must minimise the Gibbs Free energy to find the equilibrium state.

So now we can see where these thermodynamic potentials come in use. Let's consider an example next.

## Maxwell's Relations

Next, we're going to use our new thermodynamic potentials to arrive at some very useful relations.

First, we need to do a bit of setup. For a general function of two variables which has an exact differential,  $f(x, y)$ , we have that

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

as we've used many times before. Because  $df$  is an exact differential we can say that

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

If we then write

$$F_x = \left( \frac{\partial f}{\partial x} \right)_y ; \quad F_y = \left( \frac{\partial f}{\partial y} \right)_x$$

we have

$$\frac{\partial F_y}{\partial x} = \frac{\partial F_x}{\partial y}.$$

We can now use these relations on  $U$ ,  $H$ ,  $F$ , and  $G$ .

## Example using the Gibbs Free Energy

The Gibbs Free Energy is  $G = H - TS$ . As we saw earlier, this gives us that

$$dG = -SdT + VdP.$$

We can also write  $dG$  as

$$dG = \left( \frac{\partial G}{\partial T} \right)_P dT + \left( \frac{\partial G}{\partial P} \right)_T dP$$

which gives

$$S = - \left( \frac{\partial G}{\partial T} \right)_P ; \quad V = \left( \frac{\partial G}{\partial P} \right)_T$$

Let's consider the first of these statements. We can perform the following operation

$$- \left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial^2 G}{\partial P \partial T} \right)$$

We can do the following to the second statement

$$\left( \frac{\partial V}{\partial T} \right)_P = \left( \frac{\partial^2 G}{\partial T \partial P} \right)$$

Now

$$\left( \frac{\partial^2 G}{\partial T \partial P} \right) = \left( \frac{\partial^2 G}{\partial P \partial T} \right)$$

because  $G$  is a function of state ( $dG$  is an exact differential). So, we get that

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

This is one of Maxwell's relations. We can do the same analysis for the other 3 thermodynamic potentials, and we end up with the following relations

$$\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial P}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial P}\right)_S &= \left(\frac{\partial V}{\partial S}\right)_P \\ \left(\frac{\partial S}{\partial V}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_V \\ \left(\frac{\partial S}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P\end{aligned}$$

So why do we care about these? Well, Maxwell's relations allow us to relate quantities that are difficult to measure with those that are easier to measure. For example, consider the last expression. The change in volume with respect to temperature of a system at constant pressure is a trivial thing to measure - but we now know that this gives us the change in entropy with respect to pressure at constant temperature, which is a very difficult quantity to measure.

## Revisiting Heat Capacity (again)

Ok let's use one of the tricks from the last lecture to derive some more helpful quantities. First, let's start with the fundamental thermodynamic relation, which we can write as :

$$dS = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T} \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right] dV$$

If we then write  $S = S(T, V)$  we get

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

Which immediately gives

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V ; \quad \left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T} \left[ P + \left(\frac{\partial U}{\partial V}\right)_T \right]$$

Using the fact that

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V}$$

leads us to

$$T\left(\frac{\partial P}{\partial T}\right)_V = P + \left(\frac{\partial U}{\partial V}\right)_T$$

Recalling that

$$C_P - C_V = \left[ \left(\frac{\partial U}{\partial V}\right)_T + P \right] \left(\frac{\partial V}{\partial T}\right)_P.$$

(from Lecture 4), we then get

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P.$$

If we now define

$$\beta_P = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P; \quad -\kappa_T = \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T;$$

where  $\beta_P$  is the isobaric expansivity and  $\kappa_T$  is the isothermal compressibility, and use the following identity

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

which gives

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial V}\right)_T$$

Tidying up gives that

$$C_P - C_V = \frac{TV\beta_P^2}{\kappa_T}$$

These are all quantities which are easily measurable in the lab, meaning the difference in the heat capacities can be easily obtained.