

5.1: Helmholtz Energy (and The Clausius Inequality Pt. II)

Neither internal energy nor enthalpy are relevant under isothermal conditions, and we need to derive new functions of energy that have temperature as a natural variable. Previously we used Legendre transforms to accomplish this task- let's do so again!

Recall that volume and entropy are natural variables of internal energy because of how internal energy changes: $\partial U = T\partial S - P\partial V$; thus $U(S,V)$. The conjugate variable of V is $-P$ and the conjugate of S is T . In Sec. 3.3 we showed how to transform away internal energy's natural dependence on volume using a Legendre transform, whereby the natural variable times its conjugate ($-PV$) are subtracted from the original function: $U - (-PV) = U + PV$ to create a new function with pressure as a natural variable. This can be verified by examination of the change in enthalpy: $\partial H = T\partial S + V\partial P$, from which we see that the natural variables of enthalpy are S and P .

Let's use a Legendre transform to take away internal energy's dependence on entropy and place it on temperature by subtracting S times its natural variable T . Let's call this new function the Helmholtz energy A :

$$A = U - TS \quad (5.1.1)$$

To determine the natural variables of A we calculate the differential of the Helmholtz energy:

$$\partial A = \partial U - \partial(TS) = -P\partial V + T\partial S - T\partial S - S\partial T = -P\partial V - S\partial T \quad (5.1.2)$$

Consequently, Helmholtz has natural variables of volume and temperature, i.e. $A(V,T)$.

Let's take Helmholtz energy out for a ride like a stolen car to see what it can do. Recall that the change in U has the property of being the same as heat transferred so long as volume is held constant. The same is true for the change in H when the pressure is fixed. Both these facts are important because we power the planet with heat from burning things, including nuclear fuel. When we look at the change in A , it should become immediately apparent that when the temperature is constant then $\partial A = \partial w_{rev} = -P\partial V$. Thus, the change in A is the reversible work under conditions of constant temperature (its natural variable). In fact, the reason we use the letter "A" for Helmholtz energy is that it stands for "arbeit", which is German for work.

The next thing we want to show is that A is related to the total entropy change under the condition that both its natural variables (T and V) are held constant; see Sec. 4.2.1 if you forgot about how to relate energy to entropy via the Clausius inequality which is basically the 2nd Law of Thermodynamics. Regardless, we will review everything here. The Clausius inequality stipulates that the change total entropy always increases or stays the same. It is expressed as the sum of the change in the system ∂S plus surrounding entropy:

$$\partial S - \frac{\partial q}{T} \geq 0 \text{ J/K}$$

where $-\frac{\partial q}{T}$ is the change in the surrounding's entropy. If we multiply the above by $-T$:

$$\partial q - T\partial S \leq 0 \text{ J}$$

This doesn't seem to take us anywhere, so next we will both subtract and add $S\partial T$ on the left side in hoped of finding ∂A in the equation:

$$\partial q - T\partial S - S\partial T + S\partial T \leq 0 \text{ J} \quad (5.1.3)$$

We have to take a small break to derive how the change in Helmholtz energy is related to heat. First note that:

$$\partial A = \partial U - \partial(TS) = \partial U - T\partial S - S\partial T$$

and since $\partial U = \partial q - P\partial V$:

$$\partial A = \partial q - P\partial V - T\partial S - S\partial T$$

Now if volume, a natural variable of A , is held constant, then:

$$\partial A = \partial q - T\partial S - S\partial T \quad (5.1.4)$$

And now we can insert ∂A from Equation 5.4 above into equation 5.3:

$$\partial A + S\partial T \leq 0 \text{ J}$$

Like before, we appear stuck until we remember that we must hold both of A's natural variables constant, which are V and T. Holding T constant means $\partial T = 0$ K and thus:

$$\partial A \leq 0$$

Since this derivation began with $\partial S_{tot} \geq 0$ J/K (total entropy increases), the above is a statement of the exact same thing. Thus for a process to be spontaneous under conditions of constant volume and temperature then the Helmholtz energy must decrease.

Before moving on, we should consider chemical processes under constant volume. There are many examples, such as the cracking of hydrocarbons by the petroleum industry. Also the high temperature and pressure production of ammonia by the Haber-Bosch process, which is the catalytic reaction of hydrogen and nitrogen gases at 500 °C and 200 atm. You may have felt a twinge in your stomach when you read this- sounds dangerous, right? You bet; a chemist must be extremely cautious about initiating a reaction under constant volume conditions. This is because if gas is evolved and the reaction becomes hot, the pressure of the vessel may rise uncontrollably until an explosion occurs. There is a solution to the problem- don't ever do chemical reactions in closed vessels, rather, keep the pressure constant. But now we need a new definition of energy which has pressure as a natural variable.

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