

## Thermodynamic Potentials

In mechanics, the potential is the ability of a system to do work. A mass  $m$  at height  $h$  has a gravitational potential of  $mgh$  since this is the work gravity will do if the mass is released.

Something similar can be defined for Thermodynamic systems.

It is more complicated, though, since the second law of thermodynamics means conversion of heat to work is not so straightforward. But we can try! Start with Clausius entropy:

$dQ = TdS$  In reality, the amount of heat in a system is always less than this. So:

$dQ \leq TdS$  This is the Clausius inequality.

Using the first law:  $dU \leq dQ + dW \Rightarrow dW \geq dU - TdS$

Remember the sign convention for work:  $dW_{\text{env}} = -dW$

So  $dW_{\text{environment}} \leq -dU + TdS$ . In the case where entropy is fixed:

$dW_{\text{env}} \leq -dU$ : So in this case,  $U$  behaves like the gravitational potential energy described before.

But this only works since we imposed  $dS = 0$ . What about in other situations?

There exists a thermodynamic potential for different situations, for example when  $dP$  or  $dT = 0$ .

## Enthalpy

Enthalpy  $H$  is defined as:

$$H = U + PV \quad \text{This can also be written as:}$$

$$dH = TdS + VdP$$

Enthalpy is the potential for  $dU = 0$   $dV = 0$

We can derive heat capacity at constant pressure:

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p$$

So what does Enthalpy mean? A chemical reaction that releases heat ( $\Delta H > 0$ ) is exothermic. One that absorbs heat ( $\Delta H < 0$ ) is endothermic.

The Maxwell relation for enthalpy is:  $\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P$   
Enthalpy is most useful when describing systems in atmospheric pressure.

## Helmholtz Free Energy

Helmholtz Potential is defined as:

$$F = U - TS$$

This can also be written as:

$$dF = -SdT - PdV$$

Helmholtz potential is the potential for  $dP = 0$  (which gives  $dH = TdS$ )

The Maxwell relation for Helmholtz free energy is:

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

Helmholtz potential is most useful for systems maintained at constant temperature  $dT = 0$

## Gibbs Free Energy

The Gibbs Potential  $G$  is defined as:

$$G = U + PV - TS$$

which can also be written as:

$$dG = VdP - SdT$$

This potential is best applicable when describing phase transitions.

When phase 1 and phase 2 are in coexistence, any isothermal change is also isobaric. so  $dT=0$  and  $dP=0$ , which implies  $dG=0$ . So the Gibbs energy will be constant and the same for the two phases  $G_1 = G_2$ .

This lets us write:  $-S_1 dT + V_1 dP = -S_2 dT + V_2 dP$

$$(V_2 - V_1) dP - (S_2 - S_1) dT = 0$$

$$\therefore \frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} \quad \text{which is the Clausius-Clapeyron Relation!}$$

The Gibbs free energy can also be written as:

$$G = H - TS$$