

## Lecture 16: Free Energy

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Scribes: scribe-name1,2,3

## 16.1 Free Energy as a Force toward Equilibrium

For an isolated system, the entropy tends to increase. The system's entropy determines the direction of spontaneous change. But what if a system is not isolated? Now energy can pass between the system and the environment. The 2nd law still applies. However, the total entropy would be the determining factor.

Let's consider a small change in the total entropy;

$$dS_{\text{total}} = dS + dS_R \quad (16.1)$$

Applying the thermodynamic identity, we get,

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN \quad (16.2)$$

if we assume  $N$  and  $V$  is fixed, we have

$$dS_{\text{total}} = dS + \frac{1}{T}dU_R \quad (16.3)$$

Since  $T$  is in equilibrium,

$$dS_{\text{total}} = dS - \frac{1}{T}dU \quad (16.4)$$

Therefore,

$$dS_{\text{total}} = -\frac{1}{T}(dU - TdS) = -\frac{1}{T}dF \quad (16.5)$$

Finally, we come to the conclusion that the increase of  $S$  is equivalent to the decrease in  $F$ , under constant  $N, V, T$  conditions. This allows us to forget about the reservoir and just consider the free energy itself. Similarly, we can derive the relation under constant  $N, P, T$  conditions,

$$dS_{\text{total}} = -\frac{1}{T}(dU - TdS + PdV) = -\frac{1}{T}dG \quad (16.6)$$

Let me summarize these points,

1. constant  $V, T \rightarrow S$  tends to increase
2. constant  $N, V, T, \rightarrow F$  tends to decrease
3. constant  $N, P, T, \rightarrow G$  tends to decrease

Reconsider the case of burning water:  $\text{H}_2 + \frac{1}{2}\text{O}_2 \longrightarrow \text{H}_2\text{O}$

## 16.2 Various Phase Transitions

Phases: Different forms of the substance, such as liquid, gas, solid.

A phase transformation is a discontinuous change in the properties of a substance.

1st order → the discontinuous changes of properties is the 1st derivative of energy

2nd order → the discontinuous changes of properties is the 2nd derivative of energy

Some key points in the phase diagram,

1. phase boundary,
2. triple point, where solid, liquid, gas coexists
3. slope of phase boundary, ice anomaly
4. critical points, where gas and liquid are no longer distinguishable (fluid)
5. superconducting.....
6. Curie temperature

Diamond/Graphite

$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V \quad (16.7)$$

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \quad (16.8)$$

## 16.3 The Clausius-Clapeyron Relation

At the phase boundary, the material is equally stable as a liquid or a gas, so its Gibbs free energy must be the same,

$$G_l = G_g \quad (16.9)$$

Now imagine increasing the temperature by  $dT$  and the pressure by  $dP$ , in such a way that the two phases remain equally stable. Under this change,

$$dG_l = dG_g \quad (16.10)$$

Therefore, by the thermodynamic identify for  $G$ ,

$$-S_l dT + V_l dP = -S_g dT + V_g dP \quad (16.11)$$

Where  $\mu dN$  term is intentionally neglected ( $N$  is fixed). Now it is easy to solve for the slope of the phase boundary line,

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l} \quad (16.12)$$

Therefore, the slope is determined by the entropies and volumes of the two phases. Shallow/stiff. In practice, it is more convenient to write as

$$\frac{dP}{dT} = \frac{L}{T\Delta V} \quad (16.13)$$

where,  $L$  is the latent heat for converting the material from liquid to gas. And this is known as the **Clausius-Clapeyron relation**

The  $P$ - $T$  slope of the solid-liquid phase boundary is usually positive. But water is an exception. Why?  
Diamond/Graphite, (300 K, 15 kbar) .v.s (1800 K, 60 kbar)

Below 0.3 K the slope of the  $^3\text{He}$  solid-liquid phase boundary is negative, which phase is more dense?  
Which phase has more entropy?  
Solid phase is denser, and has more entropy.  
At absolute 0 K, the slope goes to 0, as  $\Delta S$  goes to 0.  
From Liquid to Solid,  $S$  has to increase.  
During adiabatic compression,  $S$  has to remain constant.  
Therefore,  $T$  has to drop. A good way to reach ultra-low temperature.

## 16.4 Homework

Problems 5.12, 5.13, 5.14, 5.21, 5.23

Problems 5.24, 5.28, 5.29, 5.32, 5.40

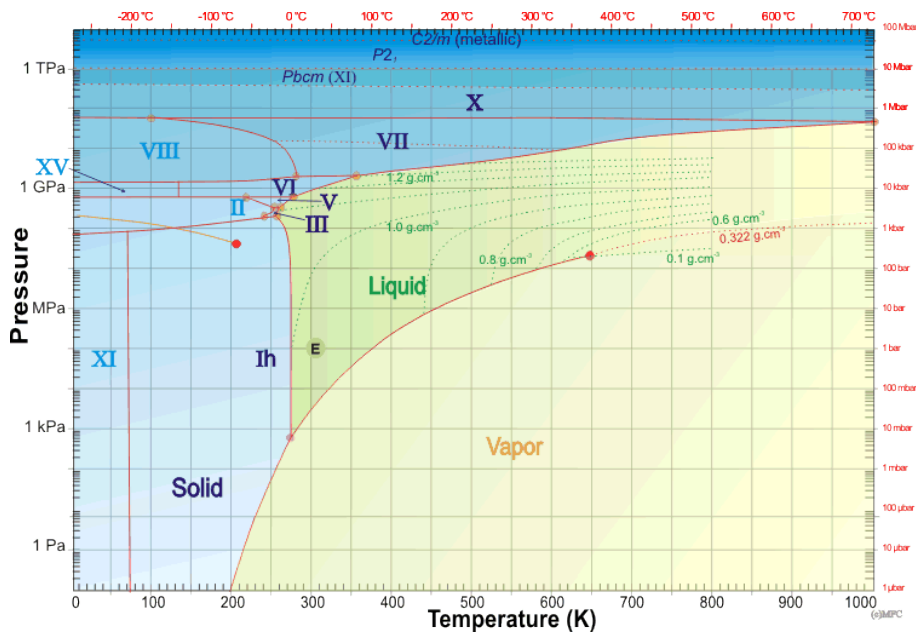


Figure 16.1: The Phase diagram for H<sub>2</sub>O.

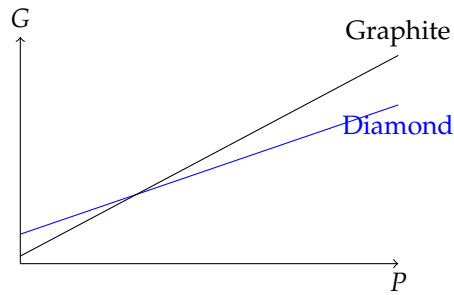


Figure 16.2: Graphite versus diamond.