

# Phase Changes & Clausius-Clapeyron Relation

-----Yanpei Deng



# Recall what is Gibbs free energy

- Gibbs free energy is defined by:

$$G=U+PV-TS$$

- If we take the derivative:

$$dG = dU + PdV + VdP - TdS - SdT$$

- Since  $dU = TdS - PdV + \mu dN$ , we get

$$dG = TdS - PdV + \mu dN + PdV + VdP - TdS - SdT = - SdT + VdP + \mu dN$$



# What if we take partial derivatives?

- We then look at the partial derivative relationships of the variables:

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

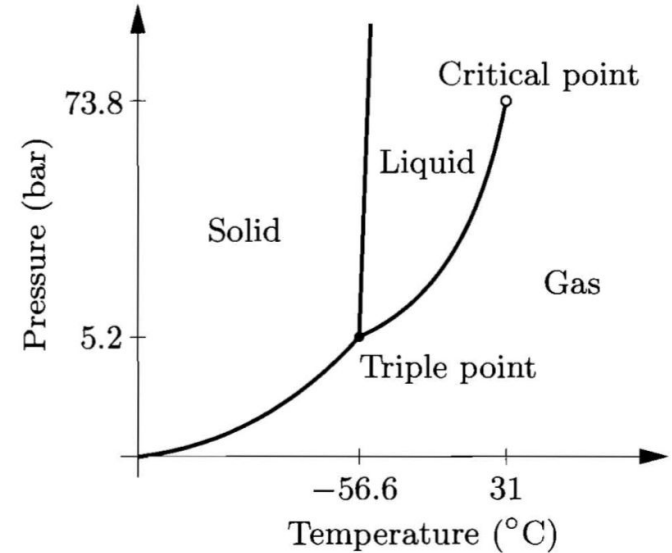
$$+V = \left( \frac{\partial G}{\partial P} \right)_{T,N}$$

$$+\mu = \left( \frac{\partial G}{\partial N} \right)_{T,P}$$

- Entropy tells us how much G changes with temperature.
- Volume tells us how much G changes with pressure.
- We maintain the temperature and pressure, then the rate of change of Gibbs Energy with particle number is  $\mu$ .

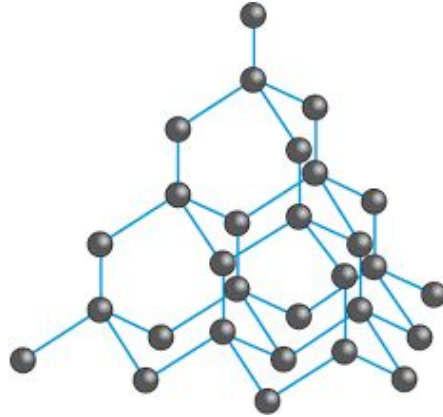
# Phase

- A **phase transformation** is a discontinuous change in the properties of a substance, as its environment is changed only infinitesimally.
- A graph showing the equilibrium phases as a function of temperature and pressure is called a **phase diagram**.
- **Triple point** is when at a certain temperature, all three phases (solid, liquid, gas) can coexist.
- As pressure increases, eventually a point is reached where there is no longer any discontinuous change from liquid to gas. This point is called the **critical point**.

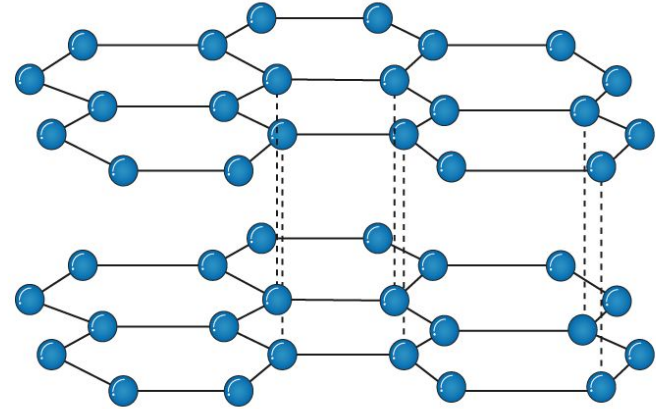


# Basic knowledge about graphite and diamond

- Graphite structure is less tightly bonded than the diamond structure
- The Gibbs free energy of a mole of diamond (at 298K and 1atm) is greater by 2900J than the Gibbs free energy of graphite
- At a given pressure and temperature, the **stable** phase is always the one with **lower** Gibbs free energy!



Diamond



Graphite

# Minimizing Gibbs free energy

$$dS_{total} = dS + dS_R$$

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

Here, the temperature and pressure for the system and the reservoir are the same. So the volume is changing while we remain the same pressure and the number of particles remains the same.

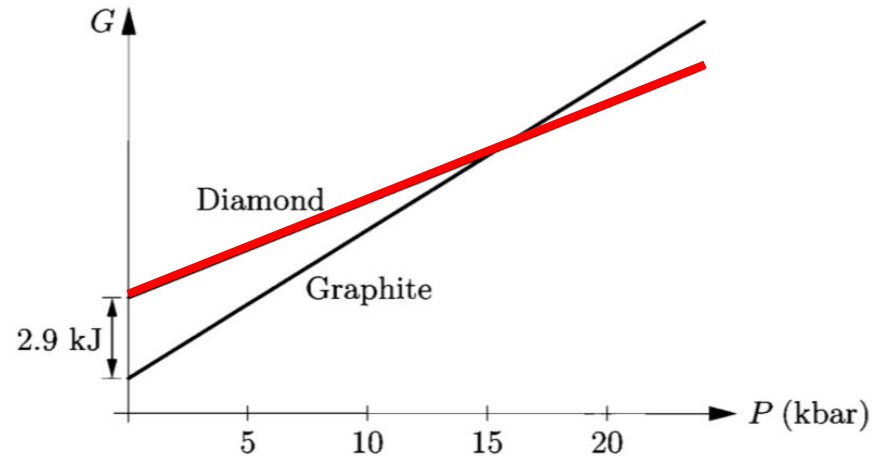
$$dS_{total} = dS + \frac{1}{T_R}dU_R + \frac{P_R}{T_R}dV_R$$

$$\blacktriangleright dS_{total} = dS - \frac{1}{T}dU - \frac{P}{T}dV = -\frac{1}{T}(dU - TdS + PdV) = -\frac{1}{T}dG$$

So as the system tends to maximize the entropy, the Gibbs free energy get minimized.

# G vs. P

- Recall that  $\left(\frac{\partial G}{\partial P}\right)_{T,N} = V$
- Since one mole of graphite has larger volume than one mole of diamond, the Gibbs free energy will grow more rapidly as the pressure increases.



# Let's calculate when diamond is more stable?

At  $P=0$ , let  $G_{\text{graphite}}=G_0$ , then  $G_{\text{diamond}}=G_0+2.9 \text{ kJ}$

The slope of diamond, denoted  $V_D=3.42 \times 10^{-6} \text{ m}^3$

The slope of graphite, denoted  $V_G=5.31 \times 10^{-6} \text{ m}^3$

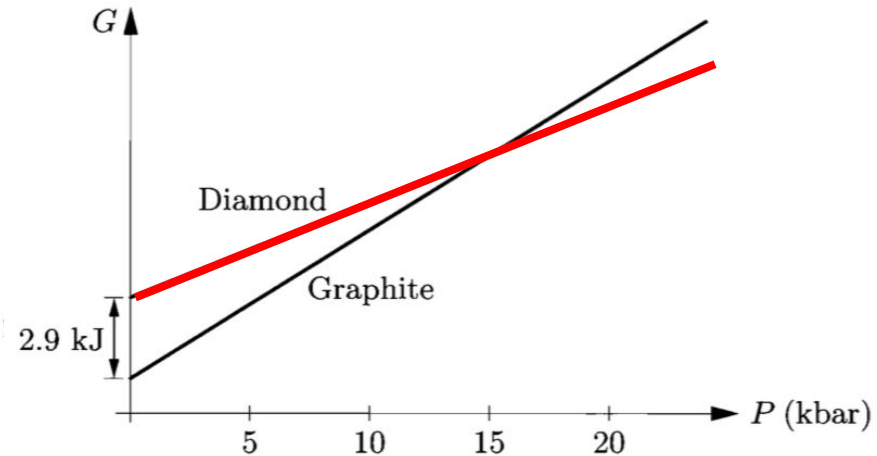
Then,  $V_D P + G_0 + 2.9 \text{ kJ} = V_G P + G_0$ . ( $G_0$  gets cancelled)

Substitute the value in,

$$3.42 \times 10^{-6} P + 2.9 \text{ kJ} = 5.31 \times 10^{-6} P$$

$$P = 1.534 \times 10^9 \text{ Pa} = 15.34 \text{ kbar}$$

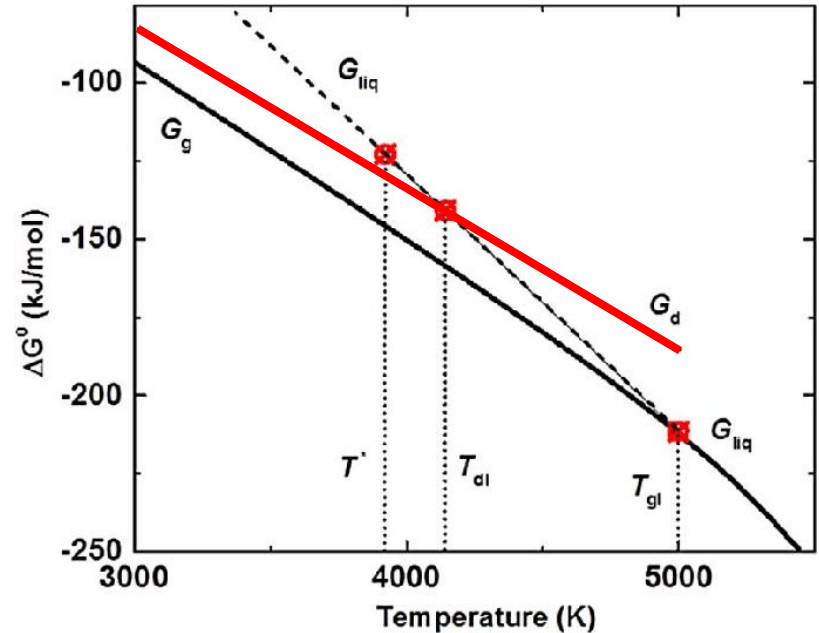
Hence, at fixed temperature, when pressure is greater than 15.34 kbar, diamond is more stable!



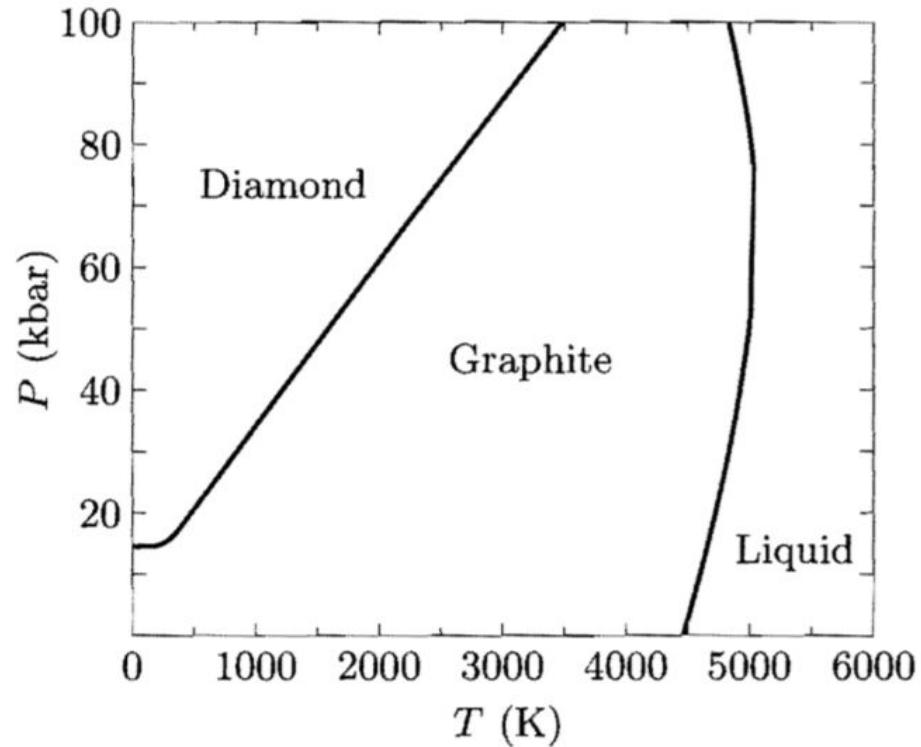


# G vs. T

- Recall that  $-S = \left(\frac{\partial G}{\partial T}\right)_{P,N}$
- The two lines have negative slopes, since  $S$  is always positive. This means that when temperature is increasing, the energy is decreasing.
- Graphite has more entropy, so as temperature increases, graphite is more stable.

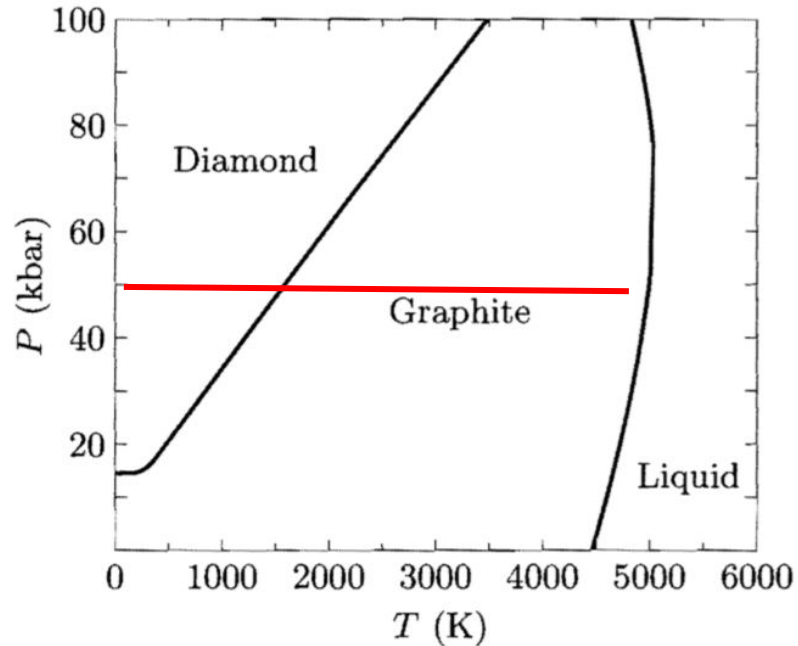


# Full phase diagram



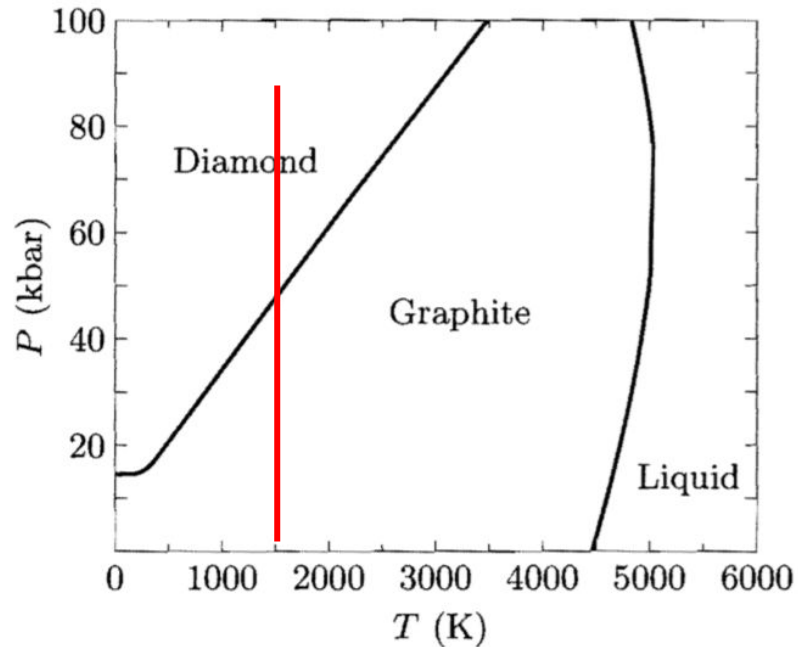
# Constant Pressure

- At constant pressure, temperature increases, graphite is more stable.



# Constant Temperature

- At constant temperature, pressure increases, diamond is more stable.



# Recall latent heat

- Latent heat is the heat needed for phase transformation to happen.
- Latent heat is defined by

$$L = \frac{Q}{m}$$

- Recall the Clausius' Relation:

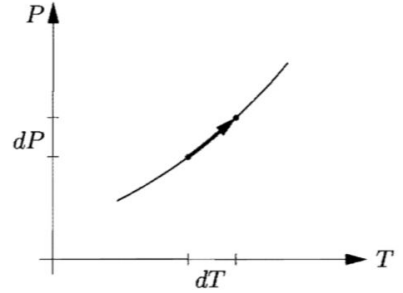
$$S = \frac{Q}{T}$$

- Therefore, we can write the entropy as:

$$S = \frac{Lm}{T}$$

# Clausius-Clapeyron Relation

- We focus on the phase boundary between a liquid and a gas
- $G_l = G_g$  (at phase boundary)
- Then we made infinitesimal changes increases in T and P, so that  $dG_l = dG_g$
- By the thermodynamic identity for G,



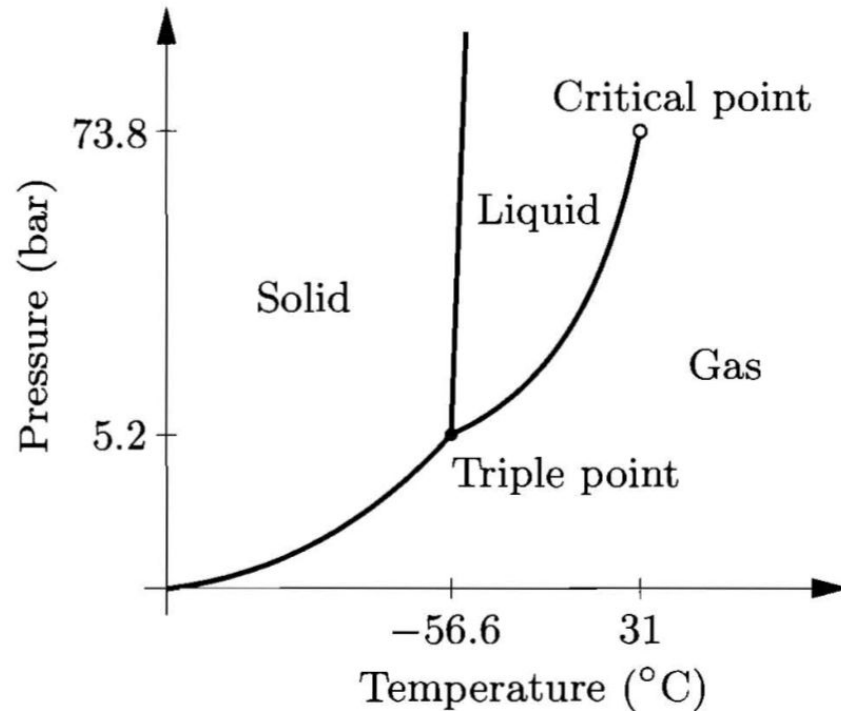
$$-S_l dT + V_l dP = -S_g dT + V_g dP.$$

- Hence,  $\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l}$
- Recall,  $S_l - S_g = \frac{Lm}{T}$
- Let  $\Delta V = V_g - V_l$
- We can conclude that

$$\frac{dP}{dT} = \frac{Lm}{T\Delta V}$$

Clausius-Clapeyron Relation and notice Schroeder's Eqn 5.47 is WRONG!!!!

# More about Clausius-Clapeyron Relation



# Thank you and... Any Questions???

Key formulae:

$$dG = -SdT + VdP + \mu dN$$

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

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

$$+\mu = \left( \frac{\partial G}{\partial N} \right)_{T,P}$$

$$\frac{dP}{dT} = \frac{Lm}{T\Delta V}$$

