

# Using Maxima to Determine the Phase Transformation from Graphite to Diamond at Atmospheric Pressure

Imagine if you could take the graphite from your pencil and transform it into diamond. In this section, we'll look at the thermodynamics of this transformation and determine via Gibbs free energy curves at what temperature this transformation would take place for atmospheric pressure. Can we turn pencil lead into diamonds on the bench-top?

As we've seen with the phases of water, we need to determine the molar enthalpies, entropies, and Gibbs free energies for the two distinct phases:

$$\bar{H}(T) = \int_{T_i}^{T_f} \bar{C}_p dT \quad (1)$$

$$\bar{S}(T) = \int_{T_i}^{T_f} \frac{\bar{C}_p}{T} dT \quad (2)$$

$$\bar{G}(T) = \bar{H}(T) - T\bar{S}(T) \quad (3)$$

The heat capacity at constant pressure for carbon is different for the two solid phases. Each phase's heat capacity is a weak function of temperature; however, we will neglect the temperature functionality since it has little effect.

The heat capacities were obtained from the CRC handbook.

$$\bar{C}_p = \begin{cases} 8.53 \frac{J}{mol K} & \text{graphite} \\ 6.12 \frac{J}{mol K} & \text{diamond} \end{cases} \quad (4)$$

We will also need reference points on which to base our plots. We use standard tables to determine that at STP,  $\bar{H}_{graphite}(T = 298 K, P = 1 atm) = 0 \frac{J}{mol}$ ,  $\bar{S}_{graphite}(T = 298 K, P = 1 atm) = 5.70 \frac{J}{mol K}$ ,  $\bar{H}_{diamond}(T = 298 K, P = 1 atm) = 1900 \frac{J}{mol}$  and  $\bar{S}_{diamond}(T = 298 K, P = 1 atm) = 2.44 \frac{J}{mol K}$ .

Using this information we will be able to develop curves for the enthalpy, entropy and Gibbs free energy as functions of temperature. The intersection of the Gibbs curves will tell us the transition temperature.

I think you can guess that the curves will either intersect at a really high temperature, or not at all.

## 1 Enthalpy vs. Temperature for Carbon

First, we will use equ. 1 combined with equ. 4 to determine the enthalpy as a function of temperature for graphite and diamond.

Keep in mind we have defined reference points above.

$$\bar{H} = \begin{cases} 0 \frac{J}{mol} + \int_{298}^T \bar{C}_p^{graphite} dT & \text{graphite} \\ 1900 \frac{J}{mol} + \int_{298}^T \bar{C}_p^{diamond} dT & \text{diamond} \end{cases} \quad (5)$$

In Maxima, we begin by defining our specific heats:

```
(%i1) Cp_g(T):=8.53$
```

```
(%i2) Cp_d(T):=6.12$
```

The subscript “\_g” refers to graphite and “\_d” refers to diamond.

Next, we will separately determine the enthalpy curves for each solid phase as well as the change in molar enthalpy for the transition ( $\Delta\bar{H}_{g\rightarrow d}$ ):

```
(%i3) H_g(T):=integrate(Cp_g(T),T,298,T)$
```

```
(%i4) H_d(T):=1900+integrate(Cp_d(T),T,298,T)$
```

```
(%i5) DH(T):=H_d(T)-H_g(T)$
```

We can now plot each of the enthalpy curves along with the change in molar enthalpy.

```
(%i6) plot2d([H_g(T),H_d(T),DH(T)], [T,298,1200], [xlabel,"Temperature (K)", ylabel,"Molar Enthalpy (J/mol)"], [legend,"Graphite","Diamond","Diamond-Graphite"]);
```

The resulting GNUplot output is shown in fig. 1. Both the graphite and diamond enthalpy curves increase; however the change in molar enthalpy curve decreases with temperature.

## 2 Gibbs Free Energy Curves for Solid Phases of Carbon

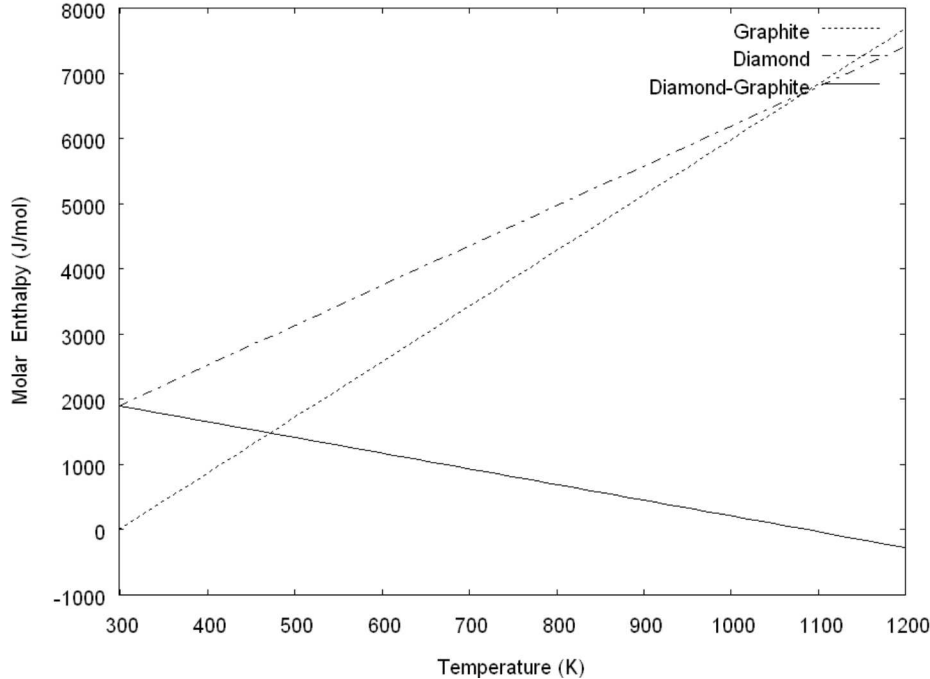
In order to determine Gibbs free energy curves from equ. 3, we first need to determine the molar entropies as functions of temperature. Using equ. 2 in combination with equ. 4 and our reference values listed above, we determine the entropy functions:

$$\bar{S} = \begin{cases} 5.70 \frac{J}{mol K} + \int_{298}^T \bar{C}_p^{graphite} dT & \text{graphite} \\ 2.44 \frac{J}{mol K} + \int_{298}^T \bar{C}_p^{diamond} dT & \text{diamond} \end{cases} \quad (6)$$

These functions combined with equ. 3 provide us with the molar Gibbs free energy curves for the two solid phases of carbon:

$$\bar{G} = \begin{cases} \bar{H}^{graphite} - T \bar{S}^{graphite} & \text{graphite} \\ \bar{H}^{diamond} - T \bar{S}^{diamond} & \text{diamond} \end{cases} \quad (7)$$

Fig. 1: Molar enthalpy as a function of temperature for the solid phases of carbon.



In Maxima we first determine our entropy as a function of temperature curves, then we determine our Gibbs free energy curves.

```
(%i7) S_g(T):=5.694+integrate(Cp_g(T)/T,T,298,T)$
(%i8) S_d(T):=2.44+integrate(Cp_d(T)/T,T,298,T)$
(%i9) G_g(T):=H_g(T)-T*S_g(T)$
(%i10) G_d(T):=H_d(T)-T*S_d(T)$
```

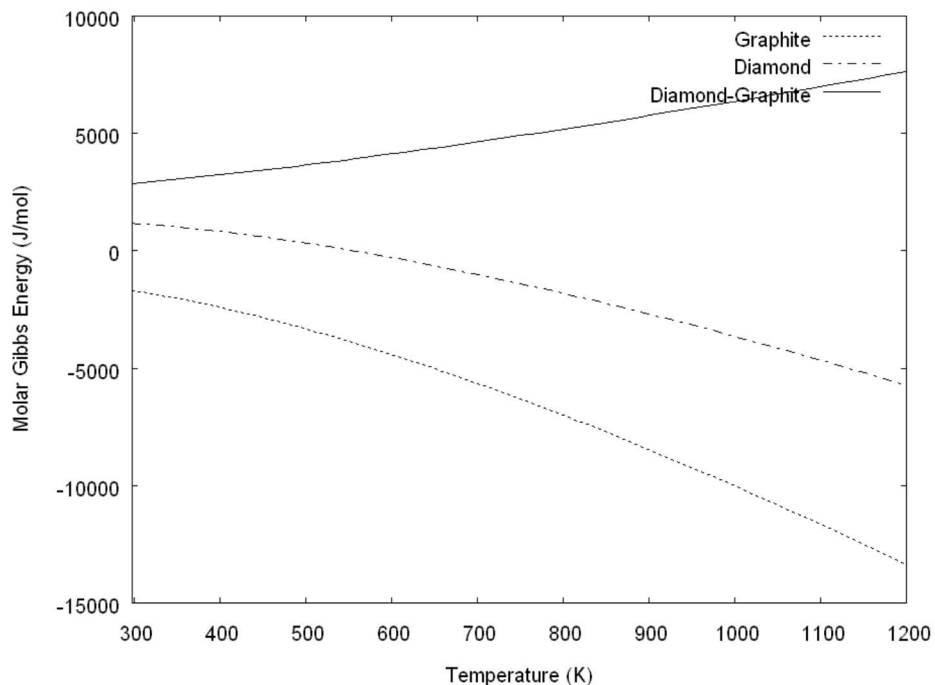
Now we can plot the Gibbs free energy curves with temperature to determine if a phase transition will occur at a reasonable temperature for our bench-top.

```
(%i11) plot2d([G_g(T),G_d(T),G_d(T)-G_g(T)], [T,298,1200], [xlabel,"Temperature (K)", [ylabel,"Molar Gibbs Energy (J/mol)"], [legend,"Graphite","Diamond","Diamond-Graphite"]];
```

The resulting GNUplot output is shown in fig. 2. For temperature ranging from 300 to 1200 K, the Gibbs curve for graphite is always lower indicating that it is the stable phase at these temperatures. Also of interest, the increasing positive  $\Delta\overline{G}_{g\rightarrow d}$  curve indicates that at no temperature within this range will  $\Delta\overline{G}_{g\rightarrow d} = 0$ , which is the necessary condition for a phase change. However, the diamond solid

De Beers is very happy that room temperature diamond is stable. So is my wife!

Fig. 2: Molar Gibbs free energy as a function of temperature for the solid phases of carbon.



phase certainly exists at room temperature. We call this a “meta-stable” phase. The only reason diamond does exist at room temperature is because the kinetics of transformation to graphite proceed very slowly at room temperature (which is a topic outside the scope of this course).

It takes pressures of about 6 GPa and temperatures of about 1200 K to manufacture a diamond.

Interestingly, if we were to expand our temperature range, we would find that graphite is *always* the stable phase for *any* temperature at 1 atm pressure. So how is diamond made? Very high pressures will shift the Gibbs free energy curves up. Since the molar volume of graphite ( $5.2 \frac{\text{cm}^3}{\text{mol}}$ ) is slightly larger than that of diamond ( $3.4 \frac{\text{cm}^3}{\text{mol}}$ ), then at high enough pressures the Gibbs free energy curves will intersect at reasonable temperatures.

The verdict: no diamonds from pencil lead will be made in our lab.