

# Determination of the Triple Point and Heat of Sublimation of Carbon Dioxide

## Introduction

The objective of this experiment is the accurate determination of both the triple point and the heat of sublimation of carbon dioxide,  $\text{CO}_2$ . Solid  $\text{CO}_2$  (dry ice) sublimates under atmospheric pressure, rather than melting. The one-component, two-phase sublimation equilibrium for carbon dioxide is represented as a chemical reaction in which the reactants and products differ only in phase:



At other pressures and temperatures, other phase transitions are possible (see the diagram in the appendix).<sup>1</sup> The one-component, two-phase vaporization equilibrium for carbon dioxide is described by



whereas fusion connects solids and liquids:



At atmospheric pressure, at no temperature does one find liquid  $\text{CO}_2$ . At the triple point, all three phases coexist. This is an invariant point – that is, for a pure substance, it only occurs at a specific pressure and temperature. As long as the three phases (solid, liquid, and gas) coexist in equilibrium, the system is fixed at the triple point (recall the phase rule:  $f = c - p + 2$ ). One can, of course, remove one of the phases (lower the value of  $p$  in the phase rule) or otherwise disturb the equilibrium and push the system off the triple point.

In this experiment, you will measure the sublimation equilibrium curve portion of the phase diagram. In addition, you will use your data points to calculate the enthalpy of sublimation for carbon dioxide. Because at a line on the phase diagram, two phases are in equilibrium, the partial-molar Gibbs energies of the two are equal along that line. This led us to derive the Clausius-Clapeyron equation<sup>2</sup> by combining our thermodynamic definition of Gibbs energy with the definition in terms of volume, pressure, temperature and entropy:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{\text{sub}}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (4).$$

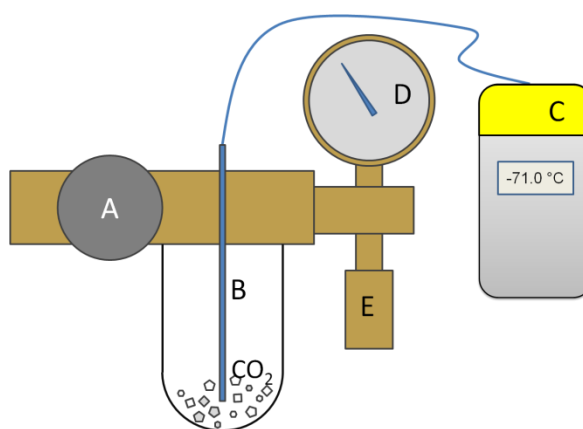
Using Eq. 4, we see that we can choose a pair of data points ( $\{P_1, T_1\}$  and  $\{P_2, T_2\}$ ), and calculate a value of  $\Delta_{\text{sub}}H$  using them. You will do this for several pairs of points, which will give you several different values of  $\Delta_{\text{sub}}H$ . Therefore, in your writeup you will need to be clear about the distinction between experimental uncertainty and statistical error.

## Experimental Procedures

In the apparatus that has been specifically designed for this experiment (based on a demonstration described in Ref. 2), pressure and temperature can be simultaneously measured and recorded at very low temperatures and high pressures. A diagram of the apparatus is shown in Fig. 1. At very low temperatures, materials can become brittle, which presents a potential safety hazard should the instrument shatter. There is both a blast shield around the device and a pressure relief valve, should the pressure exceed the pressures the system is designed to withstand.

- (1) Obtain solid  $\text{CO}_2$  and prepare it for the apparatus by crushing it into small pieces. One effective method would be to place the solid chunk of dry ice and place it into an OPEN plastic sandwich bag (by leaving the back open you allow the  $\text{CO}_2$  vapors to be released and also protect the sample from the moisture in the air). You can then use a hammer to gently break up the  $\text{CO}_2$  that is contained in the plastic bag.

- (2) Remove the plastic casing from the apparatus and make sure the gold-colored knob at the bottom of the casing is screwed tightly shut.
- (3) Fill the casing with the crushed  $\text{CO}_2$ ; keep in mind the volume of the liquid will be quite small and you need to be certain that the liquid can come into contact with the thermocouple (B).
- (4) Return the plastic casing and make sure it is tightly placed back onto the apparatus. There is an air valve (A) at the far left of the apparatus that will need to be closed to allow pressure to build up. Turn on the thermocouple gauge (C). This will be your thermometer.
- (5) You should immediately see the pressure begin to rise (D), if not, check the small gold piece at the bottom of the plastic casing; it may need to be tightened.
- (6) After allowing some pressure to build for about one minute, release the air through the valve (A) and quickly close the valve back. This will allow you to release the pressure which has built up, flushing the system so that you can start your measurements.
- (7) After closing the valve, immediately begin to take measurements of temperature and pressure. Keep track of the time between measurements in your notebook as well. At first you will need to take many data points as the P and T change rapidly, but further out fewer points will be necessary, especially at the triple point.
- (8) Once the  $\text{CO}_2$  has passed the triple point, continue to collect data as the pressure and temperature values continue to change. Once the pressure no longer increases, but the temperature continues to increase, the safety valve (E) has cracked and the experiment has ended.



**Figure 1.** The  $\text{CO}_2$  experimental apparatus. Solid  $\text{CO}_2$  is placed into the cup, sealed with valve (A). The thermocouple (B) is inserted into the  $\text{CO}_2$ , and displays the temperature on the handheld readout (C). Simultaneous measurements of pressure are made on the gauge (D), until relief valve (E) cracks.

### Pre-Lab

1. According to the figure in the appendix, what are the temperature and pressure of the  $\text{CO}_2$  triple point? Estimate the highest temperature at which you could observe any solid at 6 atm, which is approximately the limit of this experiment.
2. In our experiment, if you go beyond the triple point, will you expect to proceed along the liquid-vapor equilibrium curve or the solid-liquid curve? Explain your answer.
3. Summarize the procedures in your lab book. Be prepared to discuss with your lab partners how you will divide up the work for this lab.

### Data Analysis and Lab Reports

You do **not** need to include a table of every data point. When you have more than about ten data points, a plot is more appropriate. Therefore prepare a pressure (in atm) vs. temperature (in K) diagram of your data. Use Excel to graph your data into the form of a phase diagram. Be sure to include the experimental uncertainties in both pressure and temperature in a very brief narrative paragraph. Which is the dominant uncertainty? What other error sources exist for this experiment?

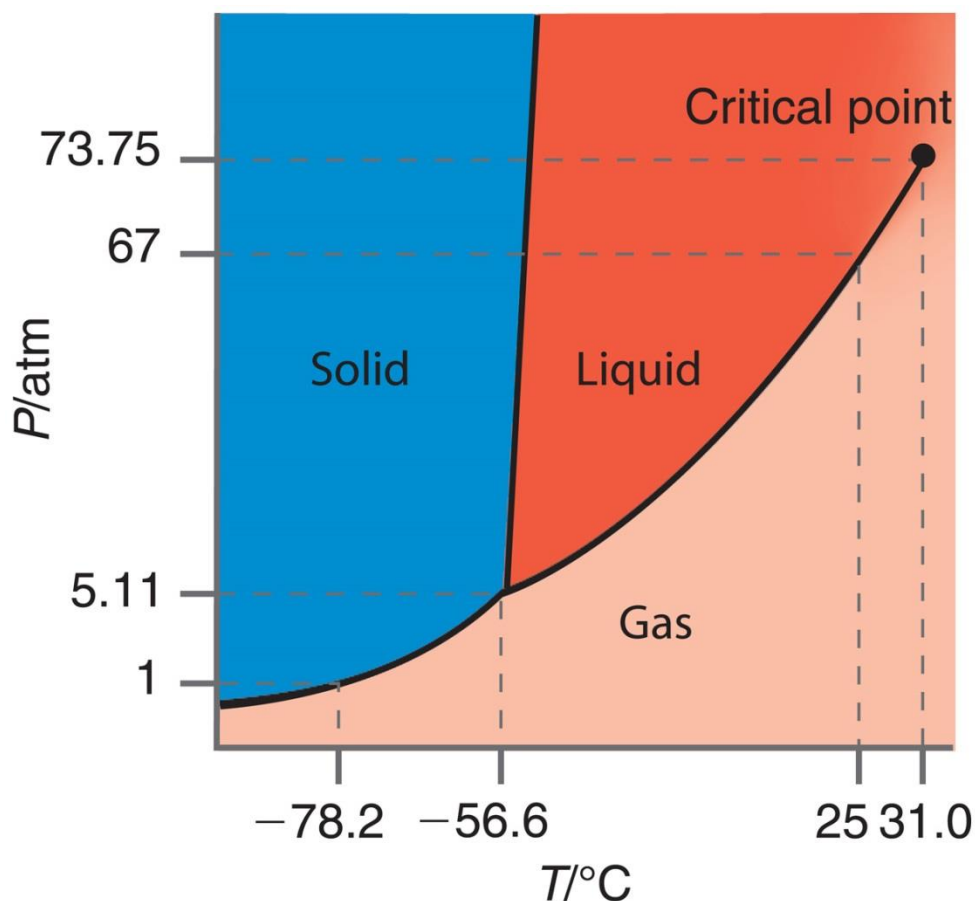
1. Determine the triple point pressure and temperature from your graph. Explain how you could determine this point based solely from the pressure and temperature data (especially if you have the timing of the points), even without observing that all three phases were in equilibrium. Include error bars (and discuss whether or not your experiments and the literature values fall with them) in both pressure and temperature based on your raw data. Compare your triple point determination to the literature values. What is your percent difference in temperature? in pressure?

2. Select 10 pairs of  $P, T$  data points (one pair means two values of  $P$ , with their corresponding values of  $T$ ) on your sublimation curve and calculate  $\Delta_{\text{sub}}H$  based on the Clausius-Clapeyron equation (Eq. 4). List the values of  $P_1, P_2, T_1$ , and  $T_2$  in a table, and the value of  $\Delta_{\text{sub}}H$  for each pair. Average your ten results for  $\Delta_{\text{sub}}H$ . Calculate a standard deviation. Compare your average  $\Delta_{\text{sub}}H$  to the literature value. Is your result (+/- the standard deviation) accurate? What is your percent difference?
3. There is an alternative to using pairs of data to calculate  $\Delta_{\text{sub}}H$ . Use the complete data (only from the gas-solid coexistence region, and justify the removal of any points at the beginning) and Eq. 8.20 of your text to construct a linear plot. What is the slope of this plot, and how can it be related to enthalpy of sublimation? Estimate the error in your value of  $\Delta_{\text{sub}}H$  based on the scatter in your plot (describe how you did this). How do your results (value and error) compare to the method used in Question 2?

## References

1. Engel, T; Reid, P. *Physical Chemistry*, 3<sup>rd</sup> Ed.; Pearson Education: Glenview, IL, 2013; pp. 181-194.
2. Lieu, V. T., "A Simple Experiment for Demonstration of Phase Diagram of Carbon Dioxide", *J. Chem. Educ.* **73**, 837 (1996).

Appendix: The phase diagram of carbon dioxide (Ref. 1).



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**Figure A-1.** The phase diagram (P vs. T) of carbon dioxide with phase transition temperatures and pressures noted.