Skills to Develop

- Explain the phase diagrams of water and carbon dioxide.
- Define and explain triple point, sublimation curve, vaporization curve, melting curve, and critical temperature and pressure.

Phase Diagrams

A diagram showing the various phases of a system is called a phase diagram. Phase diagrams for a pure compound such as phase diagrams for water and carbon dioxide are phase diagrams for a single component system. In these diagrams, pressure (P) and temperature (T) are usually the coordinates. The phase diagrams usually show the (P, T) conditions for stable phases.

Phase diagrams are useful for material engineering and material applications. With their aid, scientists and engineers understand the behavior of a system which may contain more than one component (compounds). Multicomponent phase diagrams show the conditions for the formation of solutions and new compounds. Thus, phase equilibria is still a field of research, and there is a Journal of Phase Equilibria for the publication of these research results.

At this introduction point, we take a look of the behavior of water and carbon dioxide when the temperature and pressure are changing.

Phase Diagram of Water

The phase diagram of water is shown here. It shows that at low temperature, (solid) ice is the stable phase. At moderate temperatures and high pressure, (liquid) water is the stable phase, and at high temperature and low pressure, (gas) vapor is the stable phase. Lines separate these phases. We discuss these items separately below.

The sublimation curve separates the solid from the gas. This line indicates the vapor pressure of ice as a function of temperature. The relationship can be shown in table or graph form. The diagram is a sketch, and the following table gives more accurate numbers.

<table>
<thead>
<tr>
<th>( T ) K</th>
<th>( P ) in mmHg</th>
<th>( T ) K</th>
<th>( P ) in mmHg</th>
<th>( T ) K</th>
<th>( P ) in mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>0.00025</td>
<td>261</td>
<td>1.632</td>
<td>271</td>
<td>3.880</td>
</tr>
<tr>
<td>200</td>
<td>0.0012</td>
<td>262</td>
<td>1.785</td>
<td>272</td>
<td>4.217</td>
</tr>
<tr>
<td>210</td>
<td>0.0053</td>
<td>263</td>
<td>1.950</td>
<td>272.5</td>
<td>4.40</td>
</tr>
</tbody>
</table>
The vaporization curve is a plot of (equilibrium) vapor pressure $P$ as a function of temperature $T$. The equilibrium vapor pressure at various temperatures has been carefully measured, and a detailed table can be found in the CRC Handbook of Chemistry and Physics. A simplified table is given here.

<table>
<thead>
<tr>
<th>$T$ K</th>
<th>$P$ in mmHg</th>
<th>$T$ K</th>
<th>$P$ in mmHg</th>
<th>$T$ K</th>
<th>$P$ in mmHg</th>
<th>$T$ K</th>
<th>$P$ in mmHg</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>4.579*</td>
<td>310</td>
<td>47.067</td>
<td>370</td>
<td>682.07</td>
<td>400</td>
<td>682.07</td>
</tr>
<tr>
<td>274</td>
<td>4.926</td>
<td>320</td>
<td>79.60</td>
<td>371</td>
<td>707.27</td>
<td>500</td>
<td>19848.92</td>
</tr>
<tr>
<td>275</td>
<td>5.294</td>
<td>330</td>
<td>129.82</td>
<td>372</td>
<td>733.24</td>
<td>600</td>
<td>92826.40</td>
</tr>
<tr>
<td>280</td>
<td>7.513</td>
<td>340</td>
<td>204.96</td>
<td>373</td>
<td>760.00*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>290</td>
<td>14.53</td>
<td>350</td>
<td>314.1</td>
<td>374</td>
<td>787.57</td>
<td>647</td>
<td>165467.20*</td>
</tr>
<tr>
<td>300</td>
<td>26.74</td>
<td>360</td>
<td>468.77</td>
<td>375</td>
<td>815.86</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

*Triple point 273 K, Normal boiling point 373 K, Critical point 674 K.

Note that the vapor pressures for ice and water at 273 K (0°C) are the same: 4.579 mmHg (torr). At this temperature, all three phases (ice, water, and vapor) coexist. The temperature and pressure (4.579 torr) are fixed.

At temperatures greater than 647 K, water cannot be liquified. The fluid shares the properties of gas. Thus, no vapor pressure beyond this temperature is measured. The temperature of 647 K is called the critical temperature, and the vapor pressure at this temperature is called the critical pressure.

The melting curve or fusion curve of ice/water is very special. It has a negative slope due to the fact that when ice melts, the molar volume decreases. Ice actually melts at lower temperatures at higher pressure. Most Canadians skate,
and the liquid formed between the skate and ice acts as a lubricant so that the skater moves gracefully across the ice. The skate applies a very high pressure to the ice.

**Phase Diagram of Carbon Dioxide**

The phase diagram of CO$_2$ has some common features with that of water: sublimation curve, vaporization curve, triple point, critical temperature and pressure. Of course, the $P$ and $T$ values are unique to carbon dioxide. The phase diagrams of water and carbon dioxide are compared here.

The triple point of carbon dioxide occurs at a pressure of 5.2 atm (3952 torr) and 216.6 K (-56.4°C). At a temperature of 197.5 K (-78.5°C), the vapor pressure of solid carbon dioxide is 1 atm (760 torr). At this pressure, the liquid phase is not stable; the solid simply sublimes. Thus solid carbon dioxide is called **dry ice**, because it does not go through a liquid state in its phase transition at room pressure.

The critical temperature for carbon dioxide is 31.1°C, and the critical pressure is 73 atm. Above the critical temperature, the fluid is called super-critical fluid.

To be more precise, the various points of the phase diagram are further described below. In the phase diagram of (a) \(\ce{H2O}\) and (b) \(\ce{CO2}\), the axes are not drawn to scale. In (a), for water, note the triple point $A$ (0.0098°C, 4.58 torr), the normal melting (or freezing) point $B$ (0°C, 1 atm), the normal boiling point $C$ (100°C, 1 atm), and the critical point $D$ (374.4°C, 217.7 atm). In (b), for carbon dioxide, note the triple point $X$ (-56.4°C, 5.11 atm), the normal sublimation point $Y$ (-78.5°C, 1 atm), and the critical point $Z$ (31.1°C, 73.0 atm).

**Confidence Building Questions**

1. **Referring to the figure shown here, what is the phase of water at point 1?**
   
   Hint: vapor (gas)
   
   **Skill** -
   Explain the phase diagram.

2. **How many phases are there at points 2, 4, and 8?**
   
   Hint: Since these points are on curves of phase transition, there are two phases.
   
   **Skill** -
   Describe the lines of phases transitions.

3. **What change is indicated by the line from point 1, 2, 3, 4, and 5?**
   
   Hint: Pressure increases at constant temperature.
Skill -
Explain the phase diagram.

4. **What is changing as indicated by the points 6, 4, 7, 8, and 9?**
   
   Hint: Temperature increases at constant pressure.

5. **At the conditions indicated by point 3 and 6, what is the stable phase of water?**
   
   Hint: Solid ice is the stable phase.

6. **In this sketch, what is the temperature of the triple point of water with respect to 0°C?**
   
   Hint: Higher than 0 deg. C.

**Discussion -**
Identify the triple point from the discussion given earlier.

7. **In the sketched diagram, what is the melting point of ice at exactly 1 atm?**
   
   Hint: 0 degree C.

**Discussion -**
A sketch usually emphasizes some facts.

8. **When it snows, the pressure is usually less than 1.000 atm. If the sketch of the phase diagram is true, what should be the melting point of ice?**
   
   Hint: Higher than 0 degree C.

**Discussion -**
The difference may not be very significant, but you should know the trend.

9. **On the planet X, the atmospheric pressure is 10 atm, and the normal temperature is 250 K. What is the stable phase of carbon dioxide?**
   
   Hint: liquid

Skill -
Apply the information of phase diagrams to explain a phenomenon.

10. **What is the melting point of solid carbon dioxide on the planet X whose atmospheric pressure is 10 atm?**
    
    Hint: The melting point is higher than -56.4°C.

11. **Carey uses carbon dioxide to extract an organic compound from a rock bed. He carried out the experiment at a pressure of 10 atm and 320 K. What phase of carbon dioxide is Carey using?**
    
    Hint: Carey is using a carbon dioxide super critical fluid.

**Discussion -**
Supercritical carbon dioxide is a useful fluid for the extraction of many organic compounds.
Contributors

• Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)