

# Variation of Vapor Pressure with Temperature

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You are probably familiar with the fact that air can absorb a limited amount of water vapor before becoming saturated, a limit we refer to as 100% humidity. It is also generally recognized that warm air absorbs more water vapor than cold air before becoming saturated. This is why automatic clothes dryers use heated air to carry away the water vapor.

A precise study of the amount of water that is present in air at saturation is carried out by keeping the air and liquid water in contact at a controlled temperature until no more liquid evaporates. At that point, water molecules are evaporating from the liquid at the same rate they are condensing back into the liquid, so we have a dynamic equilibrium. The water molecules in the gas phase contribute to the total pressure resulting from all the gas molecules present, and we can speak of the equilibrium vapor pressure of the water at the given temperature.

Two important generalizations can be made here. First, vapor pressure is a concept that applies to any liquid or solid that is capable of being at equilibrium with its gaseous form. We can talk about the equilibrium vapor pressure of alcohol, or mercury, or lead, or dry ice ( $\text{CO}_2$ ). Second, the equilibrium vapor pressure of a substance does not depend on whether air is present or not, or whether other gases are present. The pressure of water vapor over liquid water is the same for water in a flask that has most of the air pumped out of it before it is sealed and in a flask that is simply sealed with the air still in it. The rate at which water molecules leave and reenter the liquid is not affected by the presence of bystander molecules in the gas.

Scientists long ago measured the equilibrium vapor pressures of various substances over ranges of temperatures and found, as we would expect, that the pressure rises with increasing temperature for any substance. For instance, the equilibrium vapor pressure of water measured carefully at four temperatures is tabulated below.

## Equilibrium Vapor Pressure of Water at Four Temperatures

T(°C)	P(mm Hg)	Change in P (mm Hg)
0.0	4.58	-
10.0	9.21	4.63
20.0	17.54	8.33
30.0	31.82	14.28

The interesting point here is that, not only does the pressure go up each time we raise the temperature, but it goes up much more each time we raise the temperature by the same amount (first 4.63, then 8.33, then 14.28 mm Hg). This means that, if we plot the vapor pressure against the temperature, we should get a curve that rises faster and faster as T increases, giving us a curved line instead of a straight one. The curves resulting from such a plot for water, for ethanol, and for diethyl ether are shown in Figure 1.

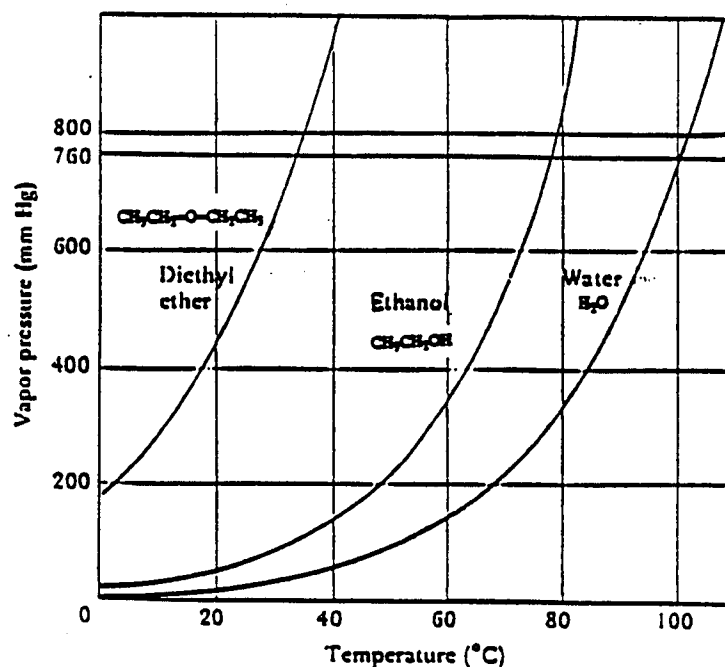


Figure 1. Equilibrium vapor pressures of three compounds, vs temperature.

We are going to discuss several aspects of these curves. One of our goals is to help you learn how to solve problems involving the relationship between vapor pressure and temperature. In the process of doing this, we will show you how we can use a simple mathematical relation to turn the curved line graph into a straight line graph. Once we have a straight line relation, finding a vapor pressure for some untabulated temperature becomes extremely easy. Another goal is to show you how these curves can be understood to result from the kinetic molecular theory, and how this understanding allows us to use the same mathematical relations for a seemingly completely different process.

Before getting into the math, let's consider how we compare the three curves in Figure 1 to each other. The curve for ethanol lies above the curve for water, which means that, at any temperature (say 60°C), the vapor pressure of alcohol is higher. This means that ethanol has a greater tendency than water to be in the gas phase. We interpret this to mean that the alcohol molecules are less strongly attracted to each other than water molecules. Similarly, diethyl ether has an even higher vapor pressure, leading us to conclude that these molecules are even less attracted to each other than ethanol molecules. These ideas are then rationalized by noting that water can form up to four hydrogen bonds to each molecule, ethanol can form up to three, and diethyl ether can't form any.

A related fact is that, if you were going to evaporate a mole of each of these liquids, it should take more heat to evaporate the water than either of the others because you must supply more energy to separate water molecules from each other (because of all those hydrogen bonds that must be broken). So the enthalpy of vaporization,  $\Delta H_v$ , should be largest for water and smallest for diethyl ether. The obvious way to get these  $\Delta H_v$  values would be to evaporate a mole of each liquid, measuring the heat used in each case. However, we shall see that there is another way to get  $\Delta H_v$ , simply by measuring the vapor pressure at two temperatures.

Notice that, at 100°C, the vapor pressure of water is 760 mm Hg, or 1.00 atm. This means that, at this temperature, the vapor being formed has a pressure sufficient to push back the atmosphere, allowing bubbles to grow and rise to the surface . . . boiling. This is why 100°C, is the boiling point of water. At any temperature less than 100°C, the vapor lacks the pressure needed to prevent the atmosphere from crushing any bubbles that even try to form. Can you estimate the boiling points of ethanol and diethyl ether? (See end of these pages for answers.)

Now we will show you how to solve numerical problems involving vapor pressure and temperature. To begin with, we simply present the formula that fits curves like these:

$$P = C \exp\left(\frac{-\Delta H_v}{RT}\right) \quad (1)$$

Here P is the vapor pressure, C is a constant (different for every substance) that carries the units of pressure (atm., mm Hg, Pascal, etc.), T is absolute temperature, R is the gas constant,  $\Delta H_v$  is our already-mentioned enthalpy of vaporization and  $\exp(\ )$  means that we are raising the number e to the power given by the quantity in the parentheses. (The number e equals 2.718, and is the base for the natural logarithms. If you don't know about e, you should seek help from your instructor.)

This formula tells you how you could calculate P for any temperature, and for any substance, if you were given the values of two numbers: C, and  $\Delta H_v$ . Pocket calculators make it very easy. But this is not the way it is generally done in chemistry. Instead, we change the formula in a way to turn it into a linear relation. Then we combine the linear formula for two different temperatures in order to eliminate the constant C. This means that we are left with only  $\Delta H_v$  as a parameter. You might wonder why we go to all this trouble instead of just using equation (1). We will explain this later.

First we make the relation linear. We do this by taking the natural log of each side of equation (1). This gives

$$\ln P = \ln C - \left(\frac{\Delta H_v}{RT}\right) \quad (2)$$

This may not look like a linear relation, but it is if we identify  $\ln P$  as y and  $\frac{1}{T}$  as x. Then

$y = mx + b$ , where m equals  $\frac{-\Delta H_v}{R}$  and b equals  $\ln C$ . In other words, if we plot the data in the

table of vapor pressure vs T as a graph of  $\ln P$  vs  $\frac{1}{T}$ , we should get a straight line with slope

equal to  $\frac{-\Delta H_v}{R}$  and intercept equal to  $\ln C$ . We show this plot for water in Figure 2.

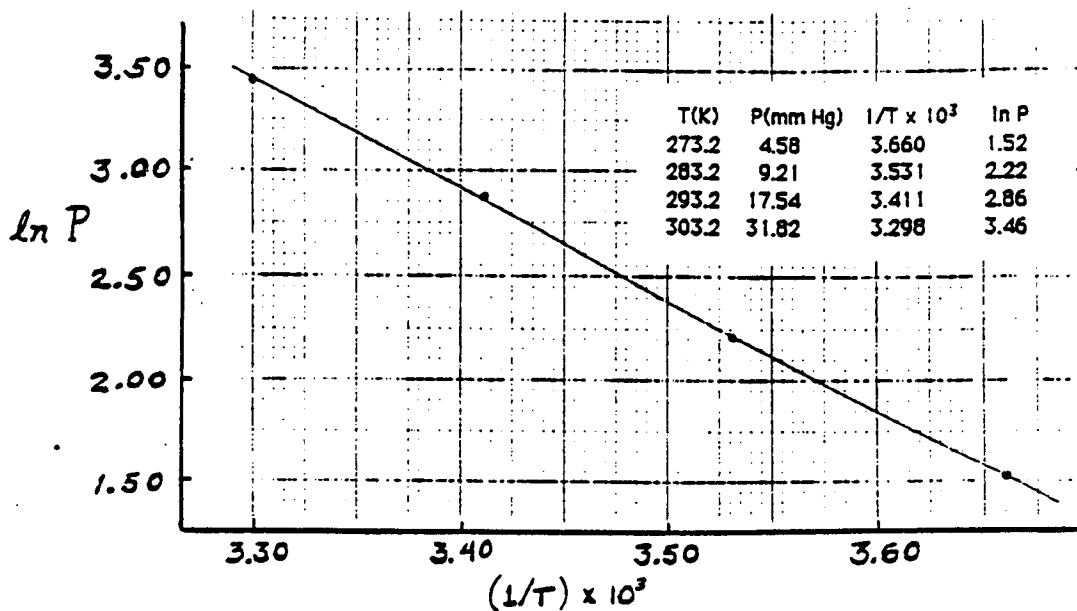


Figure 2. Plot of  $\ln P$  vs  $\frac{1}{T}$  for water.

The slope can be calculated by taking  $\frac{\Delta y}{\Delta x}$  for any two points on the line. If we take the points at 30°C and 0°C, we get

$$\begin{aligned} \frac{\Delta y}{\Delta x} &= \left( \frac{\ln 4.58 - \ln 31.82}{\frac{1}{273.2} - \frac{1}{303.2}} \right) \\ &= \left( \frac{1.52 - 3.46}{0.003298 - 0.003660} \right) = \frac{-1.94}{0.000362} \\ &= -5.35 \times 10^3 \text{ K} \end{aligned}$$

Since this equals  $\frac{-\Delta H_v}{R}$ , and  $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ ,  $\Delta H_v = 44.5 \times 10^3 \text{ J/mol}$ , or 44.5 kJ/mol.

Notice that we have arrived at a value for the enthalpy of vaporization of water from values of vapor pressure at two temperatures, as was promised.

The reason scientists prefer a linear relation is that, when they plot experimental data, they can try to find the best straight line through the (somewhat scattered) points. This is much easier than trying to find the best exponential curve through a set of points.

What we have just done is use the values of two points on a line to calculate its slope. From the slope we got  $\Delta H_v$ . Notice that we did not use the value of  $C$  when we did this. Another possibility is to take the value of the line at one point and the slope of the line to get the value at a second point. This means using the vapor pressure at one temperature together with  $\Delta H_v$  to get the vapor pressure at a second temperature. Again, we wouldn't use the value of  $C$ .

Since we are not using C, we might as well get rid of it from our equation. We can do this by taking equation (2) at two different temperatures ( $T_1$  and  $T_2$ ), with the two corresponding vapor pressures ( $P_1$  and  $P_2$ ). This gives us two equations, but they both still have the same term  $\ln C$ . If we subtract the two equations, that term cancels out, and we are left with

$$\ln \left( \frac{P_1}{P_2} \right) = \left( \frac{\Delta H_v}{R} \right) \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3)$$

This is the Clausius-Clapeyron equation, and you will find yourself using it to solve problems in this course. It embodies the linear relation of equation (2) without any dependence on C, and it is very convenient because it frees us from drawing a graph, or even thinking about a graph.

The Clausius-Clapeyron equation has five algebraic variables ( $P_1$ ,  $P_2$ ,  $T_1$ , and  $T_2$ , and  $\Delta H_v$ ) so if the values for any four of them are given, it is a simple calculation to get the missing fifth value. For example, you may be given  $P_1$ ,  $T_1$ ,  $P_2$ , and  $T_2$ , and asked to calculate  $\Delta H_v$ . Or you could be given  $\Delta H_v$ ,  $P_1$ ,  $T_1$ , and  $T_2$ , asked to find  $P_2$ . Sometimes there are some more challenging problems that are of these types but are disguised a bit so that you have to figure out how to get the P's and T's for the equation.

**Example 1.** The vapor pressure of methyl alcohol is 100. mm Hg at 21°C and 400. mm Hg at 50°C. What is the enthalpy of vaporization of methyl alcohol in this temperature range?

**Solution.** It doesn't matter which set of conditions we label "1" and which "2," so let's set

$$P_1 = 100. \text{ mm Hg}, T_1 = (21 + 273)\text{K} = 294 \text{ K}$$

$$P_2 = 400. \text{ mm Hg}, T_2 = (50 + 273)\text{K} = 323 \text{ K}$$

$$\ln \left( \frac{100.}{400.} \right) = \left( \frac{\Delta H_v}{8.314 \text{ JK}^{-1}\text{mol}^{-1}} \right) \left( \frac{1}{323\text{K}} - \frac{1}{294\text{K}} \right)$$

$$-1.386 = \left( \frac{\Delta H_v}{8.314 \text{ JK}^{-1}\text{mol}^{-1}} \right) (-.000305 \text{ K}^{-1})$$

$$\Delta H_v = 37,700 \text{ J mol}^{-1} = 37.7 \text{ kJ mol}^{-1}$$

**Example 2.** What should be the normal boiling point of methyl alcohol? Use any information you need from the previous example.

**Solution.** This problem asks more from you in the way of thought. You are expected to realize that the boiling point is the temperature at which the vapor pressure equals one atmosphere, or 760.0 mm Hg. So let us recognize right away that this temperature is what we are looking for (call it  $T_2$ ), and that the corresponding pressure,  $P_2$ , is 760.0 mm Hg. Now, if  $T_2$  is what we are solving for, we had better know the values of  $\Delta H_v$ ,  $T_1$  and  $P_1$ . We have  $\Delta H_v$ , since that is what we solved for in the previous example. As for  $T_1$  and  $P_1$ , we can use either of the sets that we used in the previous example. Let's use  $T_1 = 294$  K and  $P_1 = 100.$  mm Hg. Then

$$\ln \left( \frac{100.}{760.0} \right) = \left( \frac{37,700 \text{ J mol}^{-1}}{8.314 \text{ JK}^{-1}\text{mol}^{-1}} \right) \left( \frac{1}{T_2} - \frac{1}{294} \right)$$
$$-2.028 = 4534 \text{ K} \left( \frac{1}{T_2} - \frac{1}{294 \text{ K}} \right) = \left( \frac{4534 \text{ K}}{T_2} \right) - 15.42$$

$$\frac{4534 \text{ K}}{T_2} = 13.39$$

$$T_2 = 338 \text{ K, or } 65^\circ\text{C}$$

Some additional points should be mentioned here.

1. Because the process of taking  $\frac{1}{T_2} - \frac{1}{T_1}$  results in a very small number, it is easy for effects due to rounding at intermediate stages to get magnified. It is generally a good idea to keep your intermediate value unrounded in the calculator, rounding only at the very end.
2. Many books give the Clausius-Clapeyron equation in the form of base -10 logs instead of natural logs. This means that the left-hand side is written  $\log\left(\frac{P_1}{P_2}\right)$  and the right-hand side is divided by 2.303. Thus

$$\log \left( \frac{P_1}{P_2} \right) = \left( \frac{\Delta H_v}{2.303 R} \right) \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Since  $2.303 R = 19.15 \text{ JK}^{-1} \text{ mol}^{-1}$ , you may find the equation in some books with this mysterious looking "constant" present. (Before the days of modern pocket calculators, students worked with log tables, and base -10 log tables are easier to work with since our number system is base 10. So it made sense to work with the base -10 log version of the Clausius-Clapeyron equation. Today, that reason is gone, and you are better off using the

natural log version and avoiding the need to use the scale factor 2.303.) Be sure you use the correct button on your calculator. The log button is for base 10, and the ln button is for base e.

3. It doesn't matter whether the equation is written as  $\ln\left(\frac{P_1}{P_2}\right) = \text{etc.}$ , or as  $\ln\left(\frac{P_2}{P_1}\right) = \text{etc.}$ , just as long as the T's on the right are in the reverse order of the P's on the left.
4. Any pressure unit is OK, as long as both pressures are given in the same units.
5.  $\Delta H_v$  and R must be in the same energy units. A common error is to use kJ as the energy unit in  $\Delta H_v$  and J in R.
6. The  $\frac{1}{T_2} - \frac{1}{T_1}$  part of the calculation is conveniently handled by using the  $\frac{1}{x}$  button on your calculator.

Since it is pretty easy to make a slip in manipulating the data for this equation on your calculator, it is smart to check your answer to see if it is reasonable. Remember that (1) higher T goes with higher P, and (2)  $\Delta H_v$  must be a positive quantity since vaporization is always an endothermic process.

**Example 3.** Try to answer the following multiple choice question by inspection.

If a compound has a vapor pressure of 315 mm Hg at 42°C, which one of the following sets of data is physically plausible?

- A.  $P = 275$  mm Hg at 53°C and  $\Delta H_v = -9.3$  kJ/mol.
- B.  $P = 355$  mm Hg at 53°C and  $\Delta H_v = -9.3$  kJ/mol.
- C.  $P = 275$  mm Hg at 53°C and  $\Delta H_v = +9.3$  kJ/mol.
- D.  $P = 355$  mm Hg at 53°C and  $\Delta H_v = +9.3$  kJ/mol.

(The answer is at the end of these pages.)

**Connection of the above discussion to kinetic theory and generalization to reaction speed.**

The reason that the vapor pressure of water, say, rises as the temperature increases is that more of the molecules in the liquid have sufficient kinetic energy to overcome the attractive

forces holding them together. You have learned earlier that average kinetic energy increases in direct proportion to absolute temperature, and you have seen a graph (like the one in Figure 3) showing the distribution of energies at two different temperatures, say 20°C and 30°C. There must be some minimum energy that a molecule needs in order to escape the clutches of its comrades. Let's call it  $E_{\text{enough}}$  and mark it on the energy axis of the figure. That means that the area under the curve to the right of  $E_{\text{enough}}$  represents the fraction of molecules having sufficient energy to escape. Now suppose we increase the temperature by, say, 10°C. What happens to the average kinetic energy of the molecules? Not much. It rises by a factor of

$$\frac{303 \text{ K}}{293 \text{ K}}$$

or 3.4%. But what happens to the area under the curve to the right of  $E_{\text{enough}}$ ? It increases by a lot . . . much more than 3.4%. What happens to the equilibrium vapor pressure? Looking at the table of data for water at 20°C and 30°C that we saw on page 1, it goes up a lot too. In fact, it goes up by 81%. This is because the area to the right of  $E_{\text{enough}}$  in Figure 3 has gone up by 81%. Putting all this in other words, the ratio of vapor pressures at two temperatures is the same as the ratio of areas to the right of  $E_{\text{enough}}$  at the two temperatures.

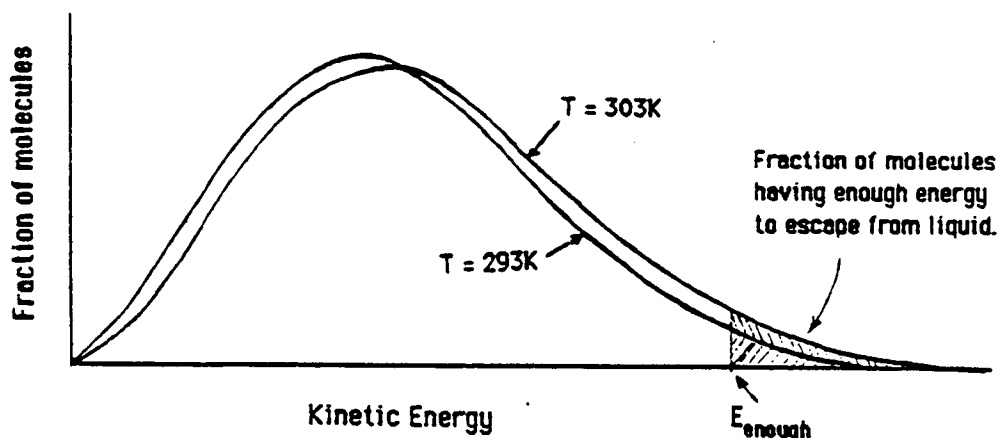


Figure 3. Kinetic energy distributions for a system at two temperatures.

Now let's do a bold thing. Let's write what we just said in words as an equation.

$$\ln \left( \frac{\text{fraction at } T_1}{\text{fraction at } T_2} \right) = \left( \frac{E_{\text{enough}}}{R} \right) \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (5)$$

By "fraction at  $T_1$ " we mean the fraction of molecules to the right of  $E_{\text{enough}}$  at  $T_1$ .

The nice thing about equation (5) is that it has generalized our understanding of vapor pressures to any situation where the rate or equilibrium is controlled by the molecules that have sufficient kinetic energy to overcome some barrier.

One example is speed of reaction. Many reactions require that reactant molecules partly break old bonds before forming new ones, and this requires a certain activation energy, often symbolized  $E_a$ . The rate constant for the reaction,  $k$ , is found to increase as the temperature increases, precisely because more molecules have sufficient kinetic energy at higher



temperature to overcome the activation energy barrier. Since the molecular energies are controlled by kinetic theory, the situation is clearly analogous to what we have for vapor pressures, so it should come as no surprise that the rate constants for a reaction at two temperatures are related by the equation

$$\ln \left( \frac{k_1}{k_2} \right) = \left( \frac{E_a}{R} \right) \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (6)$$

This equation is one version of what is called the Arrhenius equation.

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### Study Exercises

1. The vapor pressures of water at 50.0°C and at 80.0°C are 92.5 and 355.1 mm Hg respectively. Compute the value of  $\Delta H_v$  for water.  

(Ans. 42.5 kJ/mol)
2. Use your result from Exercise 1 to compute the boiling point of water at 735 mm Hg (a value often experienced in State College).  

(Ans. 99°C)
3. Carbon tetrachloride boils at 23.0°C when the applied pressure is  $1.00 \times 10^2$  mm Hg and at 57.8°C when the applied pressure is  $4.00 \times 10^2$  mm Hg. What will be the vapor pressure of carbon tetrachloride when the temperature is 15°C? (This problem requires more thought than the others.)
4. You have been led to expect that  $\Delta H_v$  for diethyl ether should be much less than that for water. Choose a couple of points from the diethyl ether curve in Figure 1 and use them to calculate  $\Delta H_v$ .  

(Ans. ~29.5 kJ/mol)
5. Can you think of a physical explanation for why  $\Delta H_v$  for water is calculated earlier in this supplement to be 44.5 kJ/mol, while in Exercise 1 it is calculated to be 42.5 kJ/mol?

(Answer to questions in text: Boiling points: ethanol, 78°C, diethyl ether, 35°C. Answer to Example 3: D.)