# The Clausius-Clapeyron Equation

Consider the following vapor pressure versus temperature data for the four liquids, water, benzene (C_6H_6), acetone ($(CH_3)_2CO$), and pentane (C_5H_{12}).

	0°C	25°C	50°C	75°C	100°C
H_2O	4.579 torr	23.76 torr	92.51 torr	289.1 torr	760.0 torr
C_6H_6	26.3 torr	95.2 torr	271.3 torr	647.8 torr	1350 torr
$(CH_3)_2CO$	70.14 torr	230.9 torr	614.3 torr	1392 torr	
C_5H_{12}	191.9 torr	531.9 torr	1231 torr		

When these data are plotted with the vapor pressure on the y-axis and temperature on the   x-axis, the following graphs are obtained.
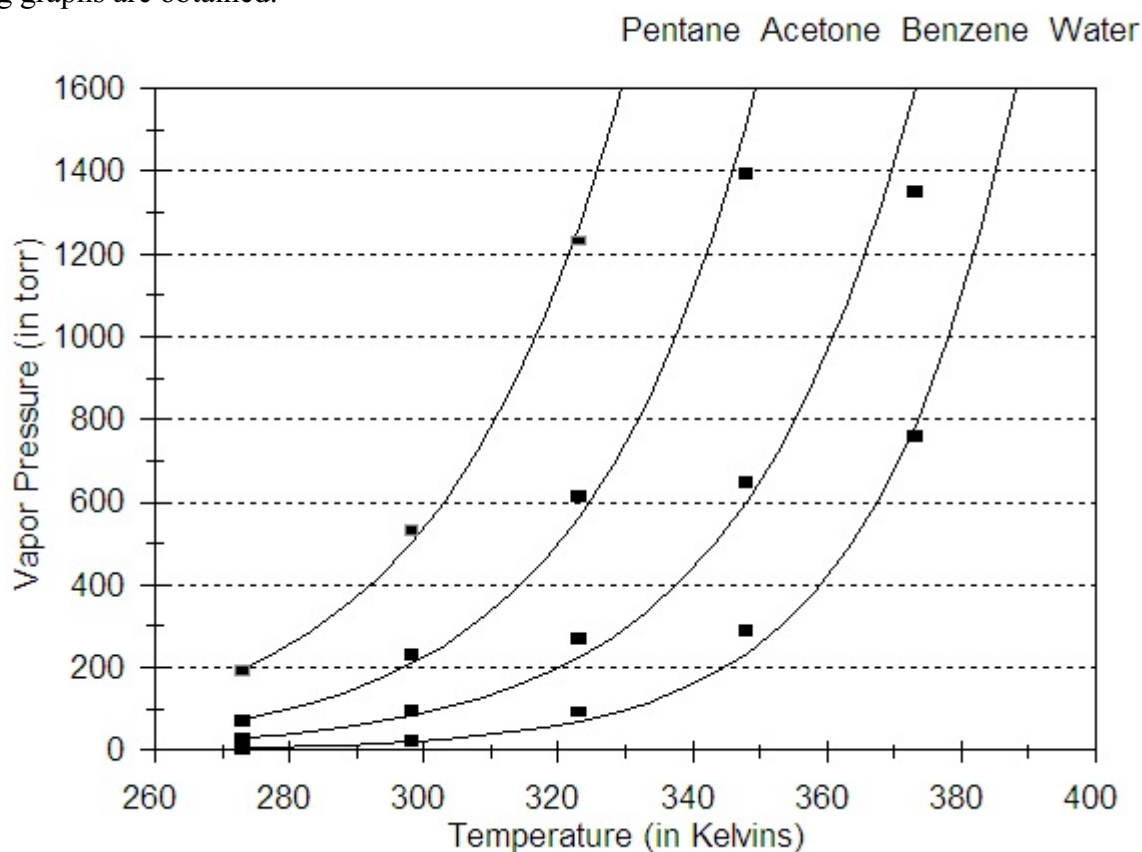
These curves are actually exponential curves with the general form of

$$P = A \left(e^{-\Delta H/RT} \right)$$ **(Eq. 1)**

where P is the vapor pressure, ΔH is the molar heat of vaporization, R is the gas constant which has a value of 8.314 J/mol·K, T is the temperature in kelvins, and A is a proportionality constant which varies from liquid to liquid.

A straight-line plot can be achieved if the logarithmic form of the above equation is used. That is, if the natural logarithm (ln) is taken of both sides of the above equation, the following is obtained.

$$\ln (P) = \ln (A) + \ln (e^{-\Delta H/RT}) = \ln (A) - \frac{\Delta H}{RT} \qquad \textbf{(Eq. 2)}$$

Equation 2 may be easily rewritten in terms of common logarithms (i.e. logarithms in base 10) since,

$$\frac{\ln (P)}{2.303} = \log (P) \qquad \textbf{(Eq. 3)}$$

Thus, if equation 2 is divided by 2.303 and then the term "log" substituted for the term "ln/2.303", the following equation is obtained in terms of common logarithms.

$$\log (P) = \log (A) - \frac{\Delta H}{2.303RT} = - \frac{\Delta H}{2.303R} \left(\frac{1}{T} \right) + \log (A) \qquad \textbf{(Eq. 4)}$$

It should be noted that equation 4 has the general form of a linear equation: $y = mx + b$.
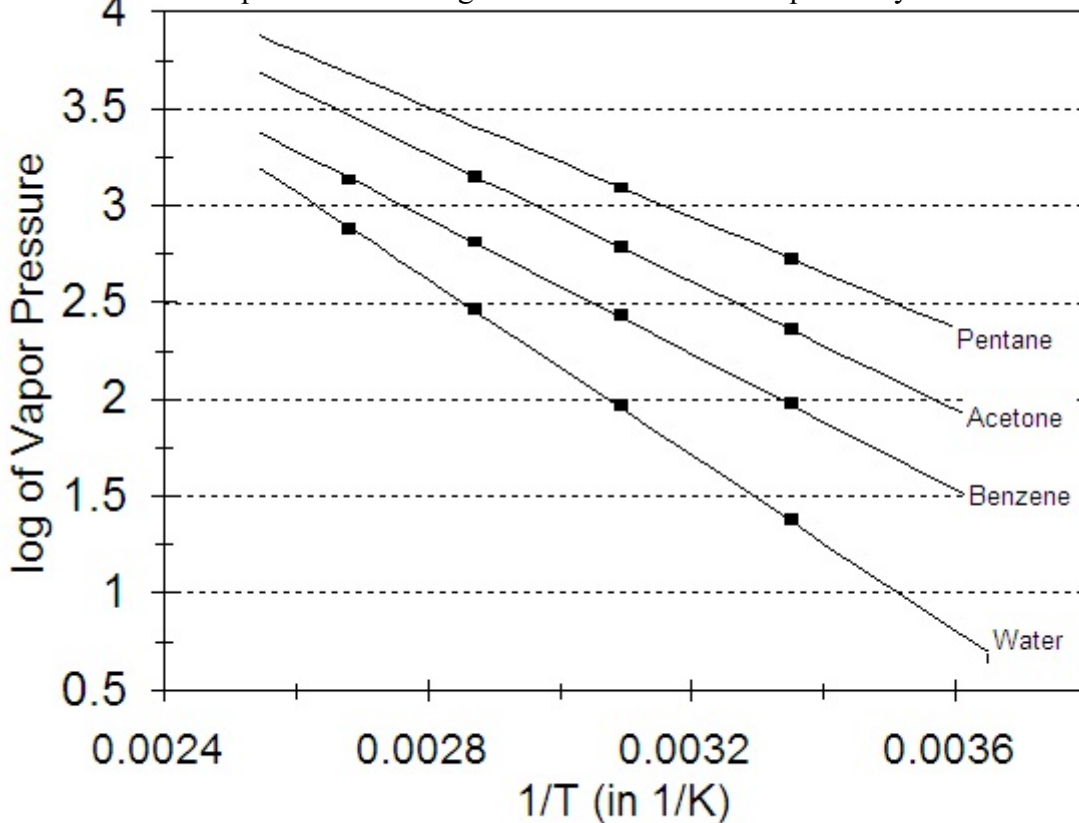
Thus, if the common logarithm of the vapor pressure (log P) is plotted on the y-axis and the reciprocal of the temperature (1/T) is plotted on the x-axis, a straight line graph is achieved with a slope of $-\Delta H/2.303R$. Using the above data and equation 4 the following graphs are obtained. Equation 4. is one form of the Clausius-Clapeyron Equation. The use of this equation requires the knowledge of the value of the constant A, which varies from liquid to liquid. However, if vapor pressure data are available at two different temperatures then an alternative form of the Clausius-Clapeyron Equation may be derived which does not require the constant A.

Since,

$$\log (P_1) = -\frac{\Delta H}{2.303R}\left(\frac{1}{T_1}\right) + \log (A) \qquad \textbf{(Eq. 5)}$$

where P$_1$ is the vapor pressure at temperature T$_1$, and

$$\log (P_2) = -\frac{\Delta H}{2.303R}\left(\frac{1}{T_2}\right) + \log (A) \qquad \textbf{(Eq. 6)}$$

where P$_2$ is the vapor pressure at temperature T$_2$,
the term, log (A), may be eliminated by subtracting the second equation from the first equation. I.e.

$$\log(P_1)-\log(P_2) = -\frac{\Delta H}{2.303R}\left(\frac{1}{T_1}\right) + \frac{\Delta H}{2.303R}\left(\frac{1}{T_2}\right) = \frac{\Delta H}{2.303R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \qquad \textbf{(Eq. 7)}$$

Finally, by using the laws of logarithms, the usual form of the Clausius-Clapeyron Equation is obtained.

$$\mathbf{log}\left(\frac{P_1}{P_2}\right) = \frac{\Delta H}{2.303R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right) = \frac{\Delta H}{2.303R}\left(\frac{T_1-T_2}{T_2\,T_1}\right) \qquad \textbf{(Eq. 8)}$$

Uses of the Clausius-Clapeyron Equation: (This equation can be used in three ways.)

1) **To determine the heat of vaporization, ΔH.**

    If vapor pressure data is known at two different temperatures (i.e., T$_1$, P$_1$, T$_2$, and P$_2$ are known), then the molar heat of vaporization, ΔH, can be estimated. This is done by rearranging (Eq. 8) to solve   for ΔH.

$$\Delta H = 2.303R\left(\frac{T_2\,T_1}{T_1-T_2}\right) \times \log\left(\frac{P_1}{P_2}\right) \qquad \textbf{(Eq. 9)}$$

    For example: The vapor pressure of pentane is 191.9 torr at 0°C (273.15 K) and is 531.9 torr at 25°C (298.15 K). The heat of vaporization, ΔH, of pentane is easily estimated by substituting these values into (Eq. 9).

$$\Delta H = 2.303\,(8.314\,J/mol{\cdot}K)\left(\frac{298.15K\times273.15K}{273.15K-298.15K}\right)\log\left(\frac{191.9\,torr}{531.9\,torr}\right) = 2.762\times10^4\,J/mol \quad \textbf{(Eq. 10)}$$

2) **To estimate the vapor pressure at a given temperature.**

If the molar heat of vaporization, ΔH, has been determined and the vapor pressure (P_1) is known at a given temperature (T_1), then the vapor pressure (P_2) can be estimated at a second given temperature (T_2). This is done by rearranging (Eq.8) to solve for log (P_2).

$$\log (P_2) = \log(P_1) - \frac{\Delta H}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \log (P_1) - \frac{\Delta H}{2.303R}\left(\frac{T_1 - T_2}{T_2\, T_1}\right) = X \quad \textbf{(Eq. 11)}$$

then taking the antilog of this quantity to give P_2.

$$P_2 = antilog\ (X) \quad\quad \textbf{(Eq. 12)}$$

For example: The vapor pressure of water is 23.8 torr at 25°C and the heat of vaporization of water is 43.56 kJ/mol. The vapor pressure of water at 50°C can be estimated by substituting the given quantities into (Eq.11) and calculating log(P_2).

$$\log(P_2) = \log(23.76\ torr)\ -\ \frac{43.56\times 10^3 J/mol}{(2.303)(8.314 J/mol\cdot K)}\left(\frac{1}{323.15\,K} - \frac{1}{298.15\,K}\right) = 1.9662 \ \textbf{(Eq. 13)}$$

Then, P_2 can be estimated by taking the antilog of 1.9662.

$$P_2 = antilog\ (1.9662)\ =\ 92.51\ torr \quad\quad \textbf{(Eq. 14)}$$

3) **To estimate the temperature where the liquid exerts a given vapor pressure.**

If the molar heat of vaporization, ΔH, has been determined and the vapor pressure (P_1) is known at a given temperature (T_1), then the temperature (T_2) can be estimated where a liquid has a second given vapor pressure (P_2). This is done by rearranging (Eq.8) to solve for $(1/T_2)$.

$$\frac{1}{T_2} = \frac{2.303R}{\Delta H}\times \log\left(\frac{P_1}{P_2}\right) + \left(\frac{1}{T_1}\right) = X \quad\quad \textbf{(Eq. 15)}$$

then, taking the reciprocal of X gives T_2.

For example: The vapor pressure of water is 23.8 torr at 25°C and the heat of vaporization of water is 43.56 kJ/mol. The temperature at which the vapor pressure of water is 40.00 torr can be estimated by substituting these quantities into (Eq.15) and calculating the quantity $(1/T_2)$.

$$\frac{1}{T_2} = \frac{(2.303)(8.314 J/mol\cdot K)}{43.56\times 10^3 J/mol}\times \log\left(\frac{23.76\,torr}{40.00\,torr}\right) + \left(\frac{1}{298.15\,K}\right) = 0.003255\,K^{-1} \ \textbf{(Eq. 16)}$$

Taking the reciprocal of $0.003255\ K^{-1}$ gives T_2.

$$T_2 = \left(\frac{1}{0.003255\ K^{-1}}\right) = 307.2\ K = 34.0\ °C \quad\quad \textbf{(Eq. 17)}$$