Module 7: Intermolecular Forces – Lecture 3

https://www.cartoonstock.com/directory/b/boiling_water.asp

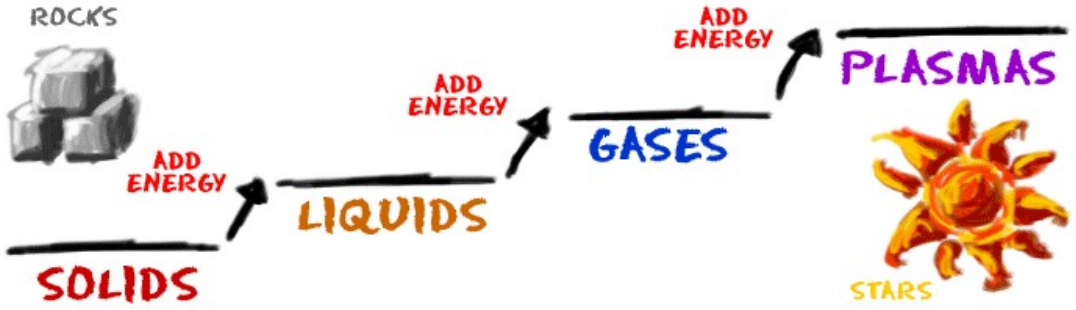
Learning Objective	Openstax 2e Chapter
Phase Changes	**10.3**
Enthalpy of Vaporization	**10.3**
Boiling Points	**10.3**
The Clausius-Clapeyron Equation	**10.3**

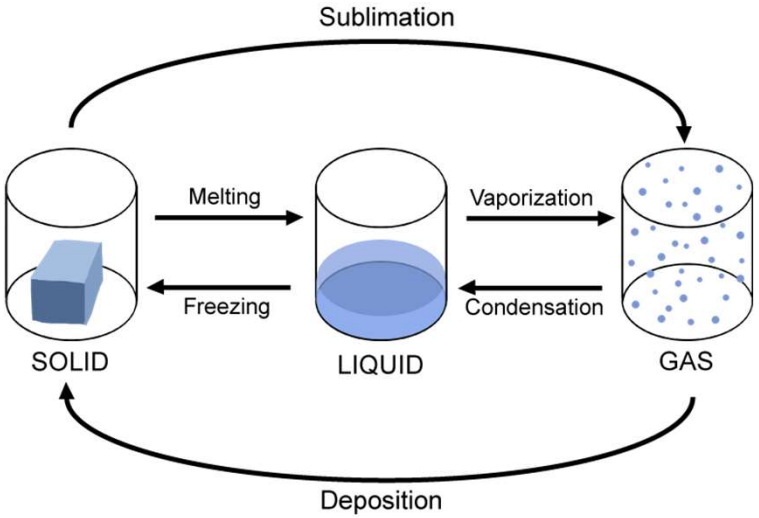
Suggested Practice Problems

Chapter 10 Exercises – Questions: 35, 37, 41, 51, 53 (a)

Answers can be found in the Chapter 10 Answer Key

Phase Changes



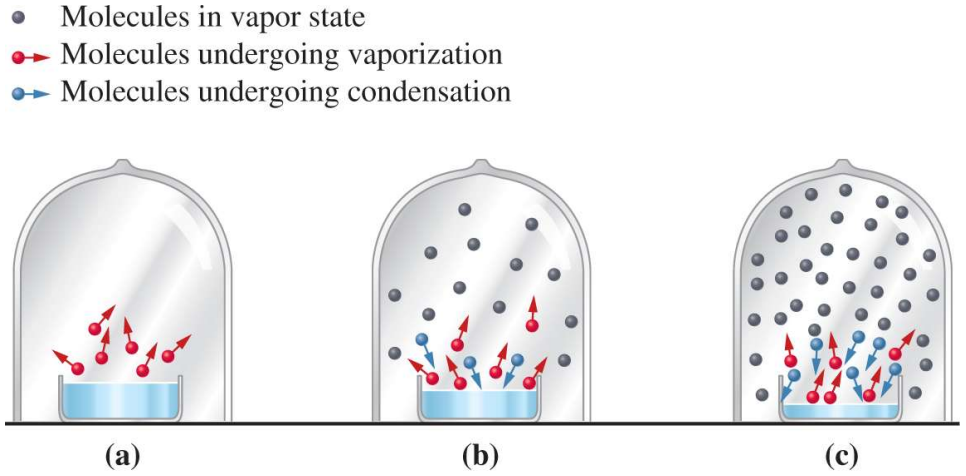


Energy transfer is required for every phase change

Enthalpy of Vaporization

Liquid-Vapour: getting to equilibrium

a) Starting with liquid phase only, liquid molecules move and collide, have a distribution of kinetic energy
   - Some liquid molecules with high kinetic energy reach surface, have enough energy to leave the liquid surface



b) Gas-phase pressure increases, gas molecules move and collide, have a distribution of kinetic energy
   - Some gas molecules with low kinetic energy collide with the surface and lose enough energy to return to the liquid phase.

c) Equilibrium: equal rates of evaporation and condensation occur. The gas pressure is known as the Vapour Pressure (P*) of the liquid.

Enthalpy of Vaporization

Why does remaining liquid feel cool during evaporation?

- The higher KE molecules in the liquid are lost through evaporation
- The average kinetic energy of the remaining liquid molecules decreases
- Liquid will cool and draw heat from surroundings as evaporation continues
- The quantity of heat required to vaporize one mole of liquid at constant temperature and constant pressure is called enthalpy of vaporization $\Delta_{vap}H$

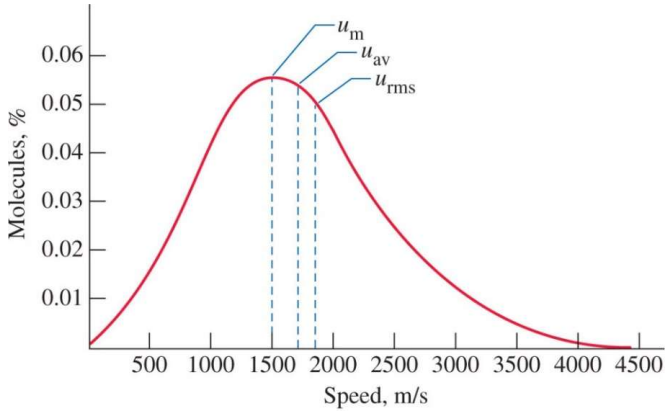


Figure 1: Distribution of molecular speeds

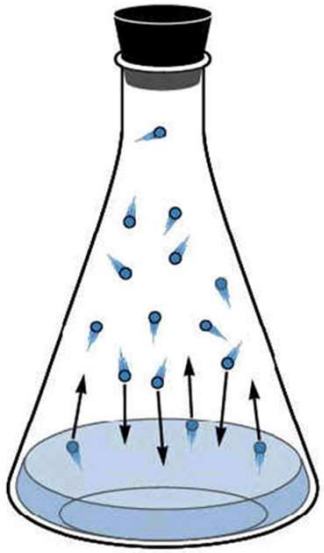
$$f(u) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} u^2 e^{-\frac{Mu^2}{2RT}}$$

Maxwell-Boltzmann Distribution

Liquid phase has similar distribution of kinetic energies

Enthalpy of Vaporization

https://www.falstad.com/gas/



liquid $\underset{\text{condensation}}{\overset{\text{vaporization}}{\rightleftharpoons}}$ vapor

Conditions for vaporization: changing the equilibrium

- Increased Temperature – more molecules have sufficient KE to overcome intermolecular forces (P* increases with higher T)
- Reduced strength of intermolecular forces
  - lower KE needed to overcome intermolecular forces

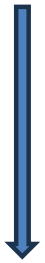
- What about Increased Surface area?
  - greater number/proportion of molecules at the surface
  - increases rate of phase change towards equilibrium but does not change the proportion of liquid and gas at equilibrium in a closed system

Enthalpy of Vaporization

- Definition of volatility?
- Liquids with “appreciable” vapor pressure at room temperature are often called **“volatile”**, while those with low vapor pressure are called **“non-volatile”**.
- This definition is arbitrary. There’s no universally accepted definition. It’s better to talk about liquids being more or less volatile by comparison.

Intermolecular Forces and Enthalpy of Vaporization

weak IMF



strong IMF

TABLE 12.4 Intermolecular Forces and Enthalpies of Vaporization at 298 K[a]

Liquid	molecular dipole μ, Debye	polarizability α, 10^{-25} cm^3	% Dispersion	% Dipole	$\Delta_{vap}H$, kJ mol^{-1}	Boiling Point, °C
Dimethyl ether, $(CH_3)_2O$	1.30	52.9	84.6	15.4	18.5[b]	–24.8[c]
Diethyl ether, $(CH_3CH_2)_2O$	1.10	102	96.3	3.7	27.1	34.5
Methanol, CH_3OH	1.70	32.9	47.6	42.4	37.4	64.6
Ethanol, CH_3CH_2OH	1.69	54.1	69.8	30.2	42.3	78.3
Water, H_2O	1.85	14.5	13.8	86.2	44.0	100

[a]All data are from the *CRC Handbook of Chemistry and Physics*, 95th edition.
[b]$\Delta_{vap}H$ values are temperature and pressure dependent (see Exercise 93). The $\Delta_{vap}H$ values for these substances at their respective normal boiling points are 21.5 kJ mol^{-1} for $(CH_3)_2O$; 26.5 kJ mol^{-1} for $(CH_3CH_2)_2O$; 35.2 kJ mol^{-1} for CH_3OH; 38.6 kJ mol^{-1} for CH_3CH_2OH; and 40.7 kJ mol^{-1} for H_2O.
[c]These are the normal boiling points, measured at 1 atm.

Enthalpy of Vaporization ($\Delta_{vap}H$) - the quantity of heat that must be absorbed to vaporize one mole of liquid at constant temperature and pressure

Enthalpy of Condensation ($\Delta_{cond}H$) - the quantity of heat that will be released to condense one mole of gas at constant temperature and pressure

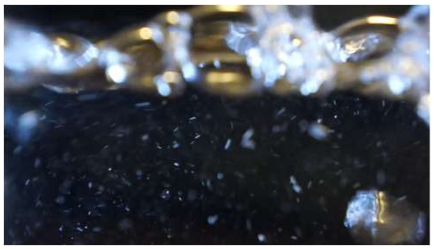
$\Delta_{vap}H$ is an endothermic process so is always positive; conversely $\Delta_{cond}H$ is always negative.

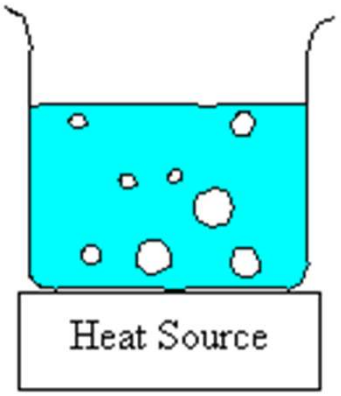
$$\Delta_{vap}H = -\Delta_{cond}H$$

Boiling

Boiling point, T_b = Temp at which $P^* = P_{atm}$

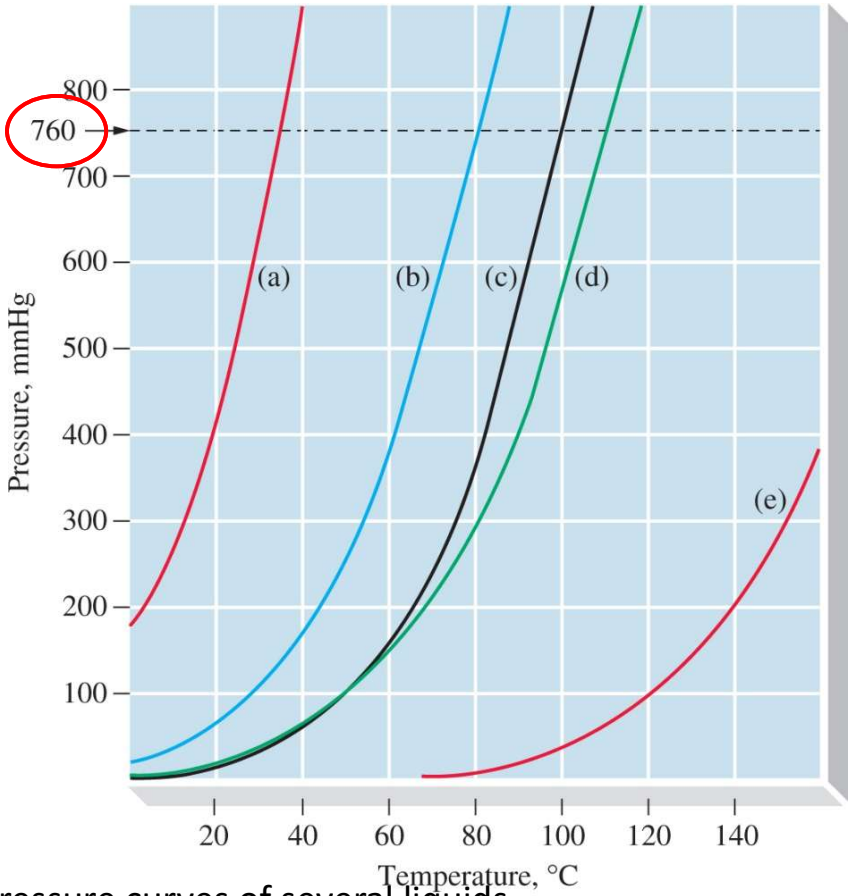
- In order to actually boil (make bubbles) T must be slightly higher than T_b so that $P^* > P_{atm}$
- Gas molecules are far apart, so intermolecular forces are now mostly eliminated.
- Liquids with higher intermolecular forces will have higher boiling points (if all else remains constant).
- Normal boiling point refers to boiling point at 1 atm = 760 mm Hg = 101.325 kPa





Vapour Pressure and Boling Point

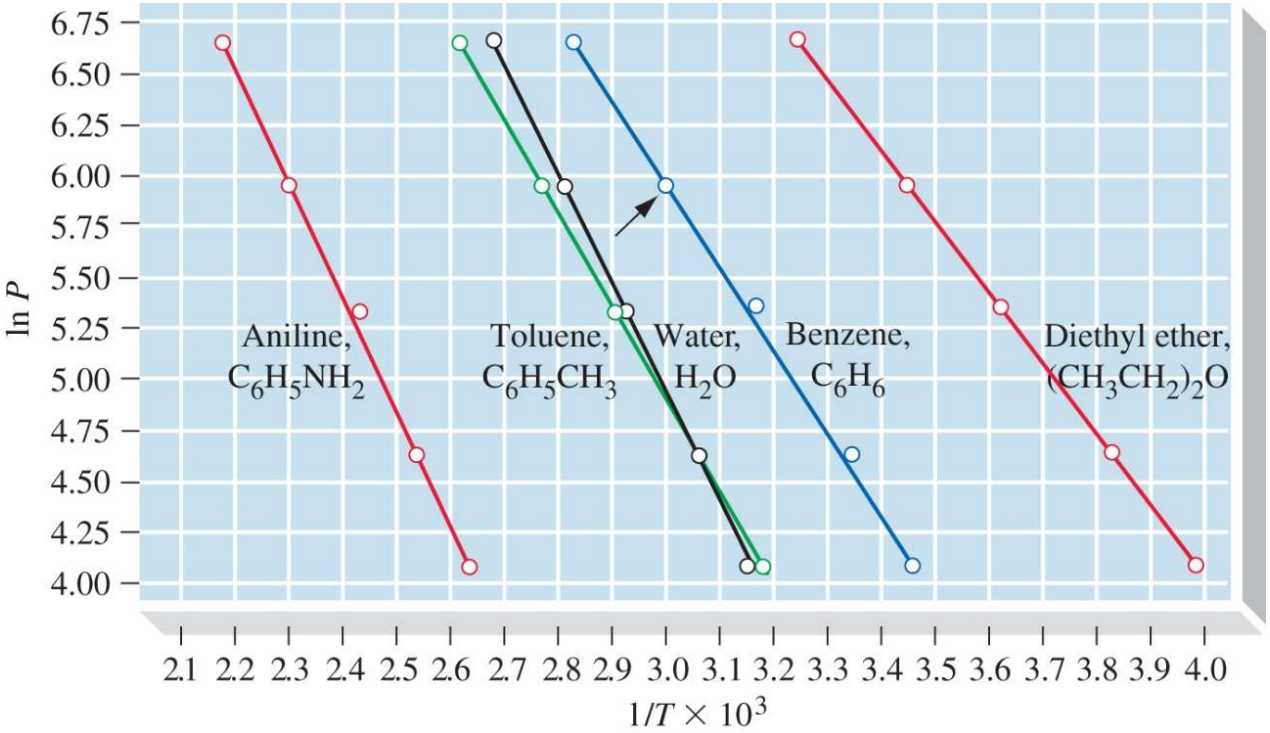
- Boiling occurs in open containers (const. P_{ext})
- Lower pressures result in lower boiling point
  - A consequence is different cooking times at different altitudes.
- When $T > T_b$ (const. P_{ext}), substance exists solely as a gas (vapour) at equilibrium
- When $T \leq T_b$ (const. P_{ext}), can have liquid and vapour at equilibrium



Vapour pressure curves of several liquids

(a) Diethyl ether, $(CH_3CH_2)_2O$; (b) benzene, C_6H_6; (c) water, H_2O; (d) toluene, $C_6H_5CH_3$; (e) aniline, $C_6H_5NH_2$; The normal boiling points are the temperatures at the intersection of the dashed line at P = 760 mmHg with the vapor pressure curves.

Clausius-Clapeyron Equation



Vapor pressure data plotted as ln(*P*) vs. 1/*T*

$$y = m\,x + b$$

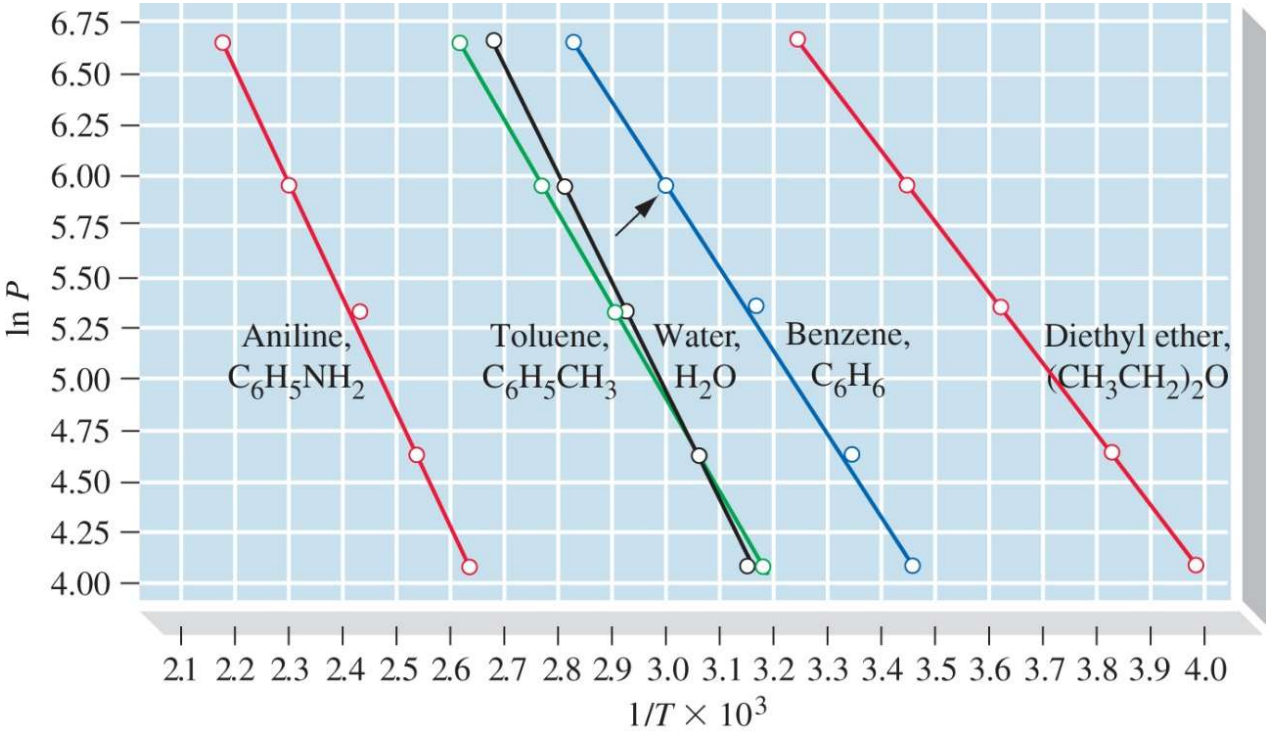
$$\ln(P) = -A\,\frac{1}{T} + B$$

$$A = \frac{\Delta_{vap}H}{R}$$

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln(P_2) - \ln(P_1) = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2}\right) + B \; - \left[-\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_1}\right) + B\right]$$

Clausius-Clapeyron Equation



Vapor pressure data plotted as ln(*P*) vs. 1/*T*

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

P_1, P_2 in any units
T in Kelvin
$\Delta_{vap}H$ in J/mol
R = 8.314 J/(mol·K)

- Describes the observed relationship between the vapour pressure of a gas in equilibrium with a liquid and the temperature of that system.

- If values for $\Delta_{vap}H$ and one pair of T and P known, can calculate P at alternate T (or T at alternate P)
- If P is measured (or known) at two temperatures, have P_1:T_1 and P_2:T_2, can calculate $\Delta_{vap}H$

Example 1: Calculation of Vapor Pressure of Water with the C.C. Equation

What is the vapour pressure (in atm) of water at 20.0°C?

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$\Delta_{vap}H = 44.0\ kJ/mol$

From definition of normal boiling point (Temp at which Vapour pressure = 1 atm, 100.0 °C)
Can set P_1 = 1 atm and T_1 = 373.15 K. T_2 = 293.15 K Convert 44.0 kJ/mol to 44 000 J/mol

$$\ln\left(\frac{P_2}{1.00\ \text{atm}}\right) = \frac{-44\,000\ Jmol^{-1}}{8.314\ Jmol^{-1}K^{-1}}\left(\frac{1}{293\ K} - \frac{1}{373\ K}\right) = -5292\ K\ x\ 0.000732\ K^{-1}$$

$\ln(P_2) - \ln(1.00) = -3.874$ $\ln(P_2) = -3.874 + \ln(1.00) = -3.874$

$P_2 = \exp(-3.874) = 0.0208 =$ **0.021 atm**

Note: for T_2 = 0.0°C = 273.15 K, get P_2= 0.0055 atm

Example 2: The normal boiling point of nitrobenzene is 210.9 °C. If the vapour pressure at 180.0 °C is 353.2 mm Hg, what is the vapour pressure at 200.0 °C?

Normally, use the CC equation to solve for P_2, but also need $\Delta_{vap}H$.

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{-\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Use extra information to calculate $\Delta_{vap}H$.

From normal B.P. info,

have P_1 = 1 atm =760 mmHg and T_1 = 210.9 °C = 484.05 K.

Can set P_2 = 353.2 mmHg and T_2 = 180 °C = 453.15 K.

$$\ln\left(\frac{353.2}{760}\right) = \frac{-\Delta_{vap}H}{8.314\ Jmol^{-1}K^{-1}}\left(\frac{1}{453.15\ K} - \frac{1}{484.05\ K}\right) \qquad -0.7663 = \frac{-\Delta_{vap}H}{8.314\ Jmol^{-1}K^{-1}}\ x\ 0.00014\ K^{-1}$$

$$-\Delta_{vap}H = -0.7663\ \frac{8.314\ Jmol^{-1}K^{-1}}{0.00014\ K^{-1}} \qquad \Delta_{vap}H = 45227\ Jmol^{-1} = 45.23\ kJmol^{-1}$$

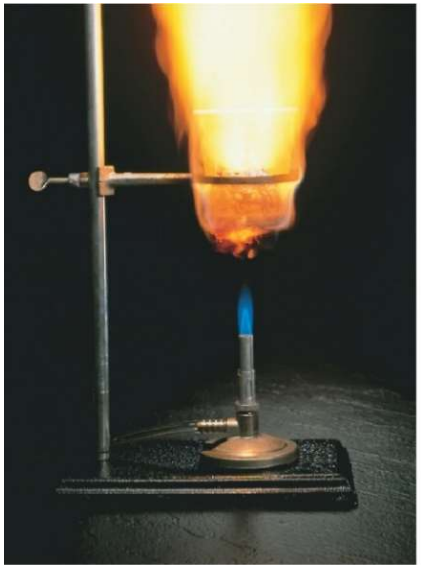
Now do usual solution with the CC equation to solve for P_2 with T_2 = 200 °C = 473.15 K.

$$\ln\left(\frac{P_2}{353.2}\right) = \frac{-45227\ Jmol^{-1}}{8.314\ Jmol^{-1}K^{-1}}\left(\frac{1}{473.15\ K} - \frac{1}{453.15\ K}\right) \qquad ln(P_2) - ln(353.2) = -5439.9\ K\ x\ -9.328x10-5\ K^{-1}$$

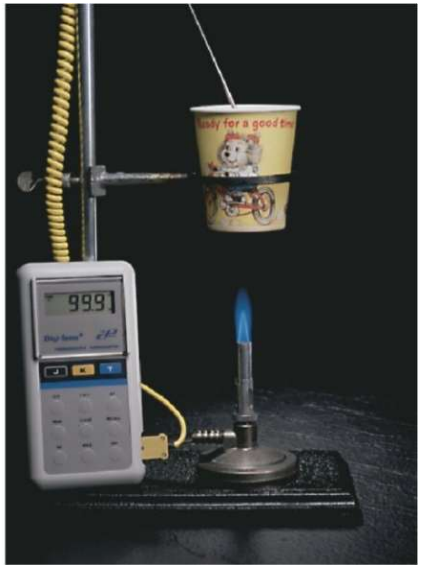
$$ln(P_2) - 5.867 = 0.50743 \qquad ln(P_2) = 6.37447 \qquad \boldsymbol{P_2 = 586.7\ mmHg}$$

Phase Changes

- Phase changes involve an exchange of energy
- Apply heat to a material at a constant rate. As it reaches a phase change, temperature remains constant even though heat is still being removed or applied.
- Why?



Empty paper cup over Bunsen burner

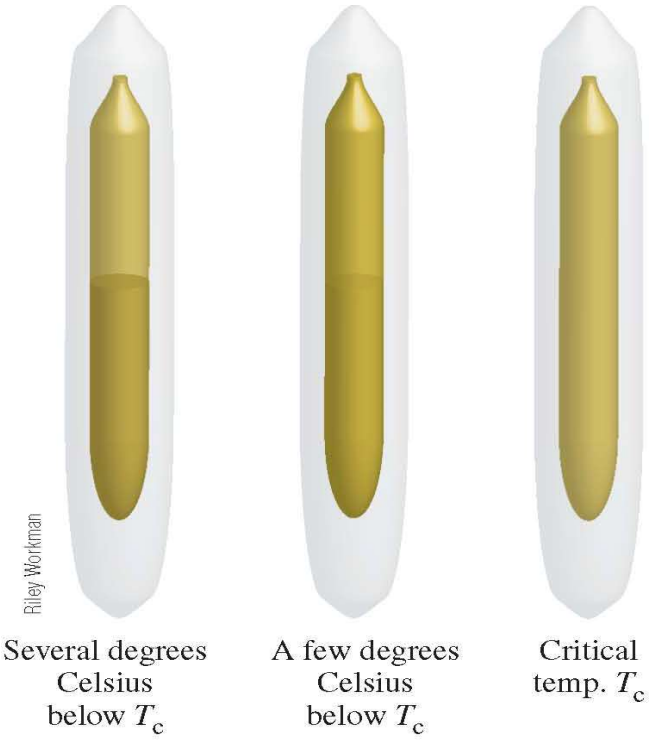


Paper cup filled with water over Bunsen burner

At the temperature of the phase change (*e.g.* boiling point of water), energy is consumed by the endothermic phase change process. As a result, the temperature remains constant even while heat is absorbed until the liquid is boiled away. More on this in the next lecture.

Critical Point: deviation from normal phase behaviour

- If a liquid is heated in a closed container
  - Density of a liquid decreases as temperature is increased
  - Density of vapour phase increases as more molecules are vaporized
  - Eventually the densities of vapour and liquid phases become equal
- The surface tension of the liquid approaches zero and the interface between vapour and liquid disappears

- Critical point: the point where liquid and vapour become indistinguishable. The temperature is called the critical temperature T_C and the pressure is denoted P_C

- The critical point is the highest point on a vapour pressure curve and represents the highest temperature at which a liquid can exist.