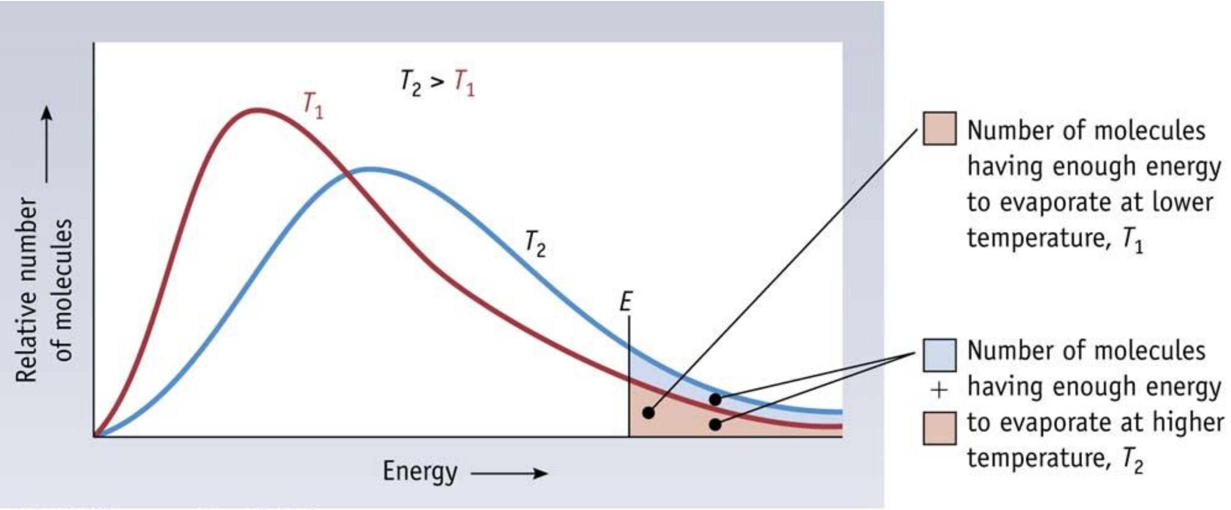
Vapour Pressure of Pure Substances

When you leave **wet dishes** overnight they will usually be **dry** the next morning.

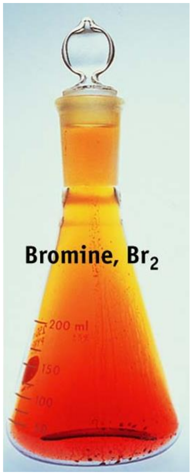
The water has evaporated – even though your kitchen was 70-80°C **below** the **boiling point** of the water. **How is this possible?**



At **any** given T, **some** molecules will have **enough** energy to escape the **intermolecular forces** holding them in the liquid phase.

Vapour Pressure of Pure Substances

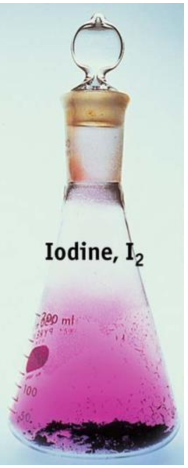
Heating a liquid **increases** the rate of **vaporization** by increasing the proportion of molecules having sufficient energy to leave the liquid state.



Since heating **increases** the extent of vaporization, this is an ______ process with a __________ **enthalpy**.

This is consistent with rapid vaporization **cooling** the remaining liquid.

The molecules at the **surface** with sufficient energy evaporate, thereby **reducing** the **average kinetic energy** of those remaining thus **reducing T**.



In a **sealed** container at equilibrium, **P** exerted by gas is the **vapour pressure**.

Vapour pressure is **not exclusive** to liquids; many **solids** have measurable $\mathbf{P_{vap}}$.

e.g. dry ice ($CO_{2(s)}$), $I_{2(s)}$

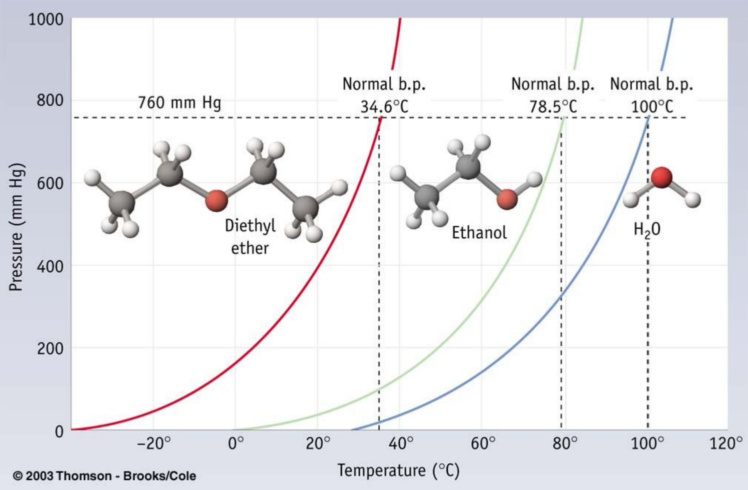
Vapour Pressure of Pure Substances

A liquid **boils** when:

P_{vap} = **Atmospheric** pressure

The **pressure** exerted by **gas = the atmospheric pressure** exerted on the liquid's surface,

boiling point is therefore **pressure-dependent**.



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Reducing the ambient **P** will **decrease** a liquid's boiling point,

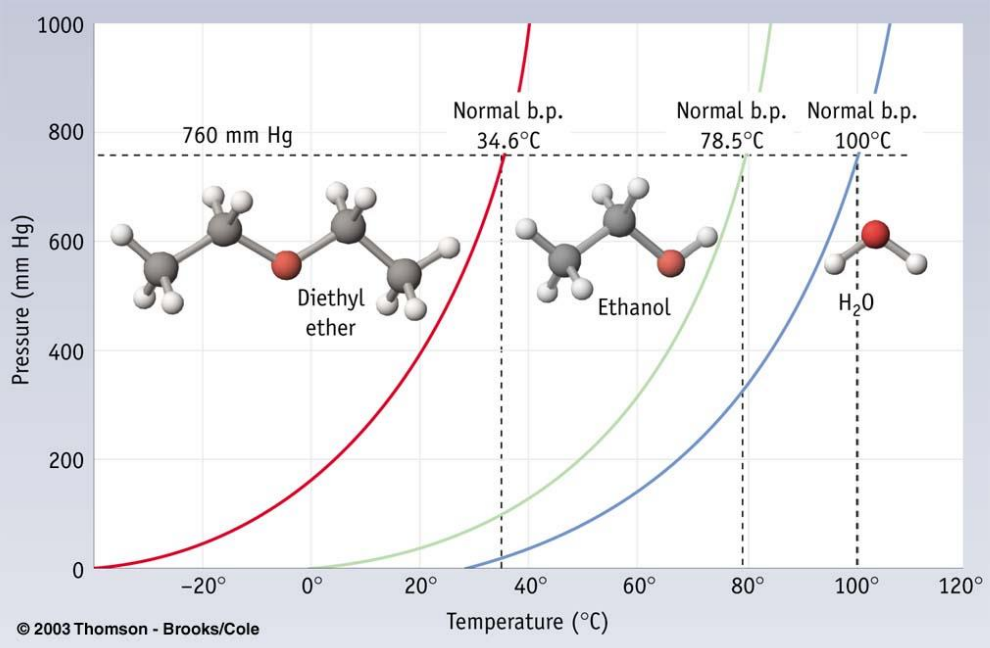
Increasing the ambient **P** will **increase** a the boiling point.

To allow comparisons of the **T** at which **P_{vap}** of a liquid is equal to ______________________ is used to define its **normal boiling point**.

Liquids with a **high P_{vap}** thus having **low boiling points** are referred to as _____________________.

Phase Diagrams

$\mathbf{P_{vap}}$ has an exponential dependence on **T**.



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$\mathbf{P_{vap}}$ can be read off directly from the $\mathbf{P_{vap}}$ **curve** or **calculated** from the free energy.

Liq ⇔ gas **K** = a_{gas}/a_{liq} = P_{gas}

K = exp(-ΔG/RT)

$\mathbf{P_{gas}}$ = exp(-ΔG/RT)

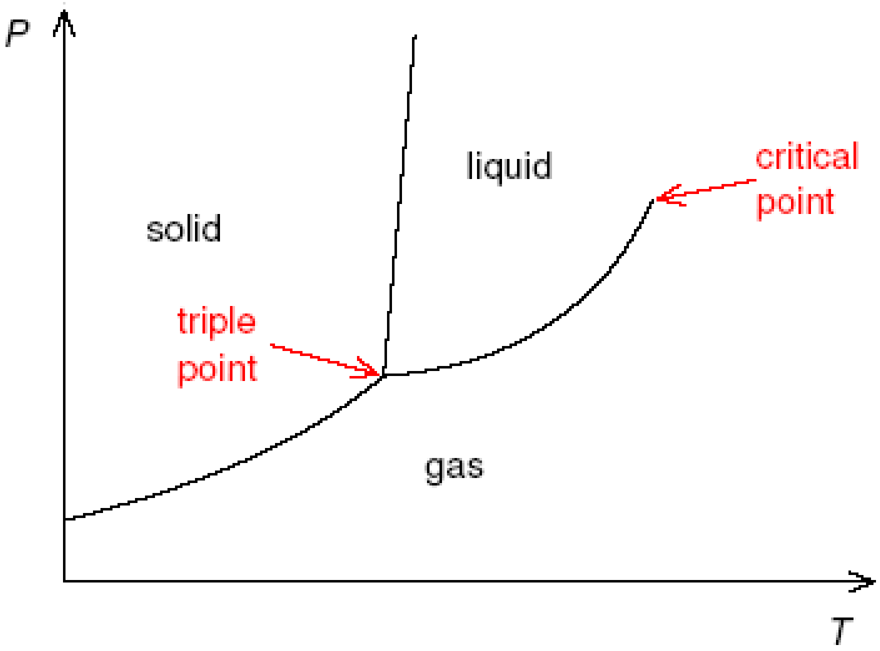
e.g. The **ΔGº** for the evaporation of water is +8.5 kJ/mol.

This curve is part of a **phase diagram**, a figure which shows the most thermodynamically stable phases under different conditions.

For pure substances, **temperature-pressure** phase diagrams are common.

Phase Diagrams

A complete **temperature-pressure** phase diagram is shown below:

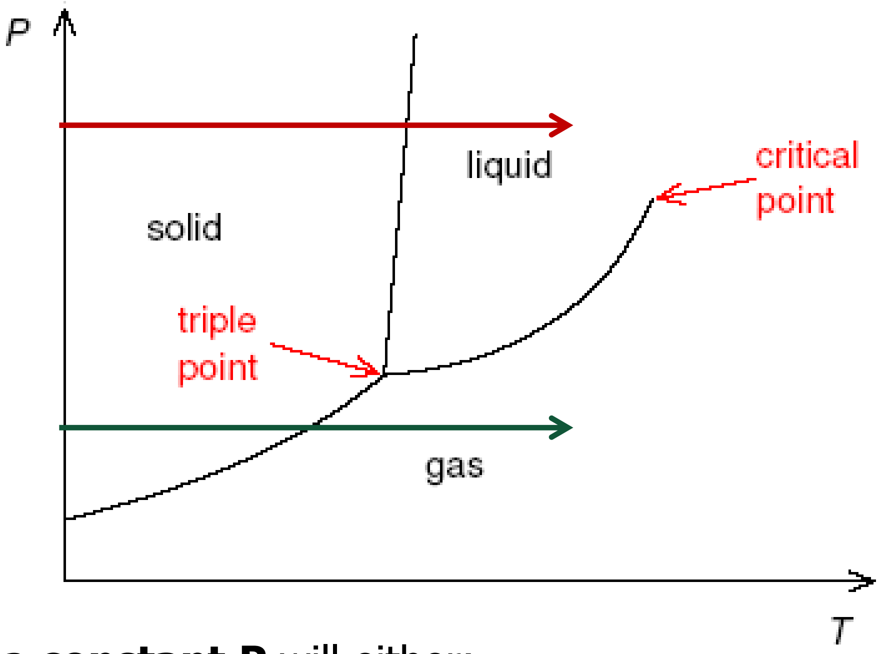


Each **curve** shows the conditions under which **two phases are at equilibrium**.

The **triple point** shows the conditions under which **all three** phases are at equilibrium!

At P’s and T’s **below** the triple point, the **liquid** phase does not form and the substance **sublimes** from gas to solid (or solid to gas).

Phase Diagrams



A **solid heated** at a **constant P** will either:

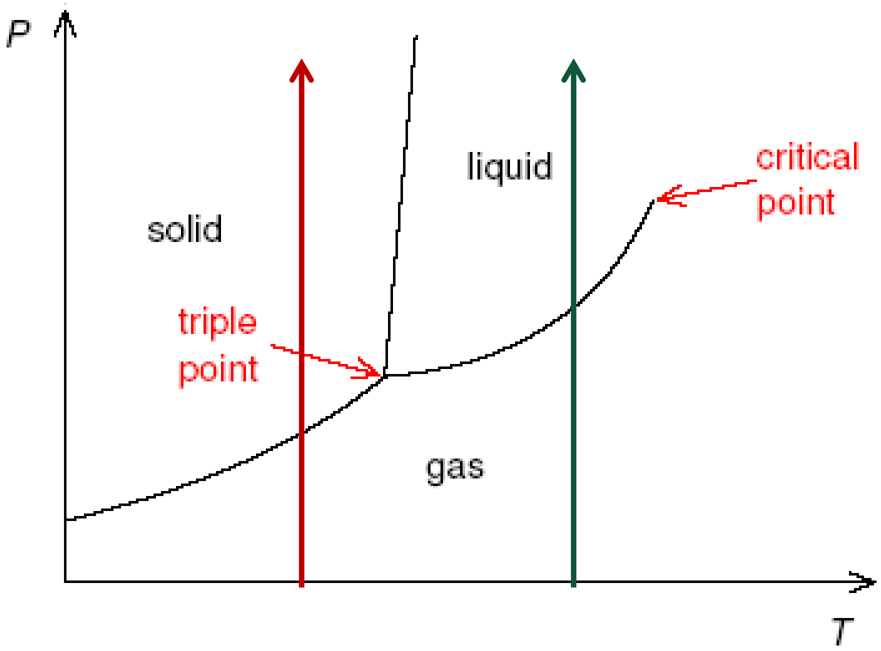
Undergo ______________________ to a liquid,

or

Undergo _____________________________ to a gas.

Which occurs depends on the _________________________.

Phase Diagrams



A **gas** at constant **T** will undergo ___________to either a **liquid** or a **solid**.

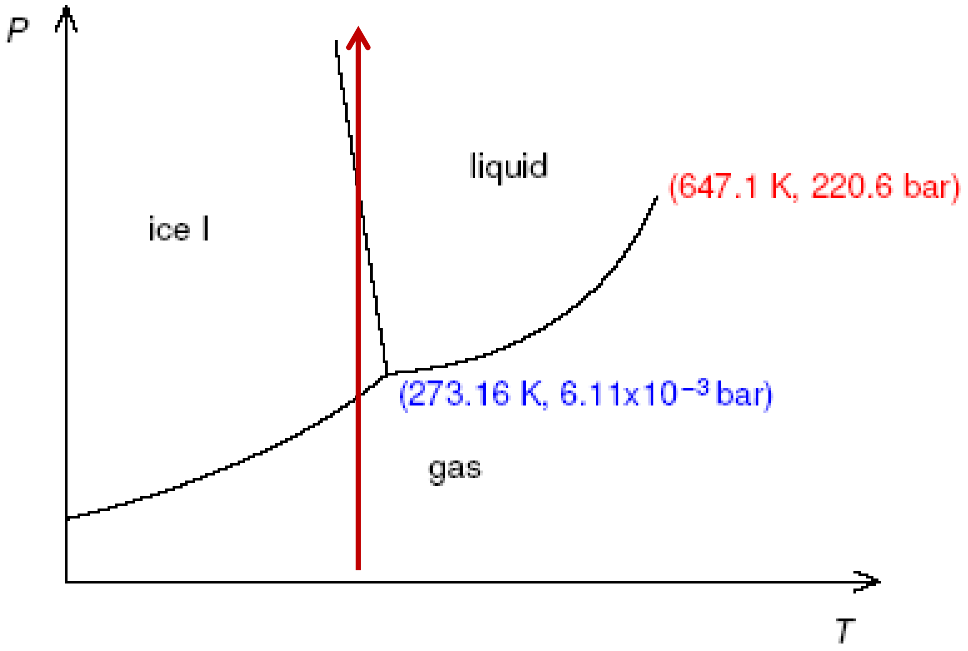
Which occurs depends on the ________________________.

This is a normal temperature-pressure phase diagram:

Where the line between the solid and liquid phases has a **positive** slope.

What does that indicate about the substance?

Phase Diagrams



The temperature-pressure phase diagram for **water** is **not normal**:

where the line between the solid and liquid phases has a **negative** slope.

What does that indicate about water?

Vapour Pressure of Solutions

The **surface** of the **pure water** consists **entirely** of water molecules, a fraction of which have enough energy to evaporate.

The **surface** of the **salt water** consists primarily of water molecules but also **some ions** from the salt.

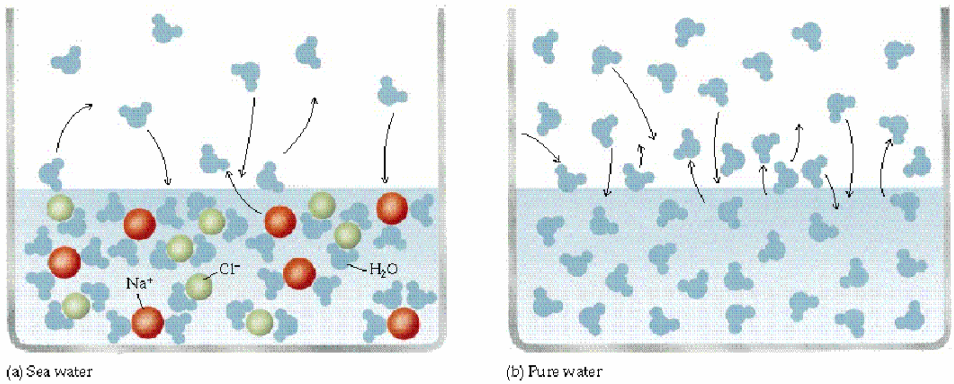
The **same fraction** of water molecules has enough energy to evaporate but, since **fewer** water molecules are on the surface**, fewer** evaporate.

Essentially, the salt ions **block access to the surface.**

As a result the salt water has a **lower P_{vap}** than the pure water.

Thus it will need to be heated to a **higher T** to raise its **P_{vap}** to equal to atmospheric P.

Hence the **boiling point** of salt water is **higher** than that of pure water.



Vapour Pressure of Solutions

Raoult's law defines the vapour pressure of a solvent (**A**):

$$P_A = X_A P_A{}^{\circ}$$

P_A is the vapour pressure of the **solvent** (in solution)
$P_A{}^{\circ}$ is the vapour pressure of the solvent (as a pure liquid)
X_A is the mole fraction of the solvent molecules.

n.b. Raoult's law **only** calculates the vapour pressure of the **solvent**.

If a **solute** is volatile, it will have a vapour pressure **too**:

$$[A] = k_H P_A$$

[A] is the concentration of the volatile solute **A**,
P_A is the vapour pressure of the volatile solute and
k_H is the Henry's law constant (solute-specific).

This is **Henry's law**. It is usually presented when discussing solubility of gases.

Equilibrium Constant and Temperature

An equilibrium constant (K) is only constant with **constant temperature**. Why?

The **enthalpy** and **entropy** change for a reaction vary **slowly** with temperature;

however, the **free energy** change is **strongly** temperature-dependent:

At any temperature:

$$\Delta G = \Delta H - T\Delta S$$

Hence, as **ΔG** changes with T, **K** changes accordingly

$$\Delta_r G_m^o(T) = -RT\ln[K(T)]$$

Equilibrium Constant and Temperature

For a reaction at temperatures $\mathbf{T_1}$ and $\mathbf{T_2}$, the following can be stated:

$$\Delta_r G_1^o(T_1) = \Delta_r H^o - T_1 \Delta_r S^o = -RT_1 \ln[K_1]$$

and

$$\Delta_r G_2^o(T_2) = \Delta_r H^o - T_2 \Delta_r S^o = -RT_2 \ln[K_2]$$

Assuming that $\mathbf{\Delta H}$ and $\mathbf{\Delta S}$ don't change significantly over the given temperature range:

$$\frac{\Delta_r H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \ln K_2 - \ln K_1$$

or:

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta_r H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Equilibrium Constant and Temperature

$\mathbf{K_w}$ = 10^{-14} under standard conditions :

$a_{H+} * a_{OH-} = 10^{-14}$

since $a_{H+} = a_{OH-}$

implies $a_{H+} = 10^{-7}$

Hence neutral water have pH 7 at 25 °C.

What is K_w at 37.00 °C?

$$\Delta_f H°(OH^-_{(aq)}) = -230.0 \frac{kJ}{mol}$$

$$\Delta_f H°(H_2O_{(l)}) = -285.8 \frac{kJ}{mol}$$

ΔH_r^o= 55.8 kJ/mol

What does this tell us about the pH of water at 37.00 °C?

$$pH = -\log(a_{H^+})$$

Kw = $2.38*10^{-14}$

pH = 6.81

Equilibrium Constant and Temperature

The atmospheric pressure in Lethbridge is typically **90 kPa**.

What is the **boiling point** of water on a typical day in Lethbridge?

At sea level the **bp** of water is 100 °C and the atmospheric pressure is 101.3 kPa.

Therefore:

P_1 = 101.3 kPa T_1 = 373.15 K

P_2 = 90 kPa T_2 = ?

$$\Delta_{\text{vap}} H_m{}^{\circ}(H_2O) = 40.66 \frac{kJ}{mol}$$

Also

$K = a[H_2O_{(vap)}]/a[H_2O_{(liq)}] = \{P[H_2O_{(vap)}]/P_{stp}\}/1 = P[H_2O_{(vap)}]$ No units

Therefore:

$K_1 = 101.3$ and $K_2 = 90$

96.75 °C

Equilibrium Constant and Temp. (Solutions)

Saturated salt solutions which freeze below 0 °C.

Calculate the **freezing point** of $NaCl_{(aq)}$ prepared by dissolving 6 mol NaCl in 1 kg H_2O.

The freezing point of pure water is 0 °C

Also:

$$K = a[H_2O_{(solid)}]/a[H_2O_{(liq)}] = 1/X(H_2O)$$

$T_1 = 273.15$ K $\qquad K_1 = 1/X_1 = 1/1 = 1$ (pure water)

$X_2 = \text{mol } H_20 /(\text{mol } H_20 + \text{mol NaCl}) = 55.\ 6 \text{ mol}/(55.6 + 6 \text{ mol}) = 0.902$

Therefore:

$T_2 = ?$ $\qquad K_2 = 1/X_2 = 1/0.902 = 1.108$

$$\Delta_{\text{fus}} H_m°(H_2O) = 6.007 \frac{kJ}{mol}$$

Exothermic!!!

-10.19 °C