- 1. Consider the phase diagram on the right.
- (a) D lies at the critical point the end of the liquid-gas line. Beyond this point, the gas cannot be liquefied by increasing the pressure.
- (b) F lies at the triple point the pressure and temperature at which the solid, liquid and gas are all at equilibrium.
- (c) The solid and gas are in equilibrium along the line H F
- (d) $G \rightarrow C$ corresponds to gas \rightarrow liquid: condensation
- (e) Solid and liquid are at equilibrium at point B.
- (f) **Point F is the triple point: solid, liquid** and gas are all at equilibrium.

2.





Statement (a) is correct.

If the density of the solid is greater than that of the liquid, the liquid occupies a greater volume and increasing the pressure favours formation of the solid. The gradient of the line separating solid and liquid is positive as the normal melting point occurs at higher T and P than the triple point. Therefore, increasing the pressure does indeed favour the solid.

Statement (b) is correct.

At 11 °C, only the solid and gas can exist. At 835 mmHg, the solid exists and at 85 mmHg, the gas exists. As the pressure is reduced, sublimation occurs.

Statement (c) is incorrect.

At P = 835 mmHg and T = 13 °C, the solid exists. At P = 835 mmHg and T = 81 °C, the liquid exists. Therefore melting occurs along this temperature change.

3. **Dispersion and dipole-dipole.**

Dispersion forces are present in all molecules. CH₃Cl possess a dipole moment with δ - chlorine and δ - hydrogen.

- 4. Hydrogen bonding. This interaction is strong in water and ice. In ice, this leads to an ordered structure with each oxygen covalent bonded to 2H and H-bonded to 2H in a roughly tetrahedral arrangement. In liquid water, some of these H-bonds break enabling other water molecules to enter the space left and acting to decrease the volume.
- 5.
- (a) In a face centred cubic lattice, there are atoms on each corner and at the centre of each face, but there is no atom at the centre of the cube.

The atoms on the corners are shared between 8 cells so 1/8 is located in this cell. The atoms on the corners are shared between 2 cells so 1/2 is in this cell. The total number of atoms in the cell is therefore:

$$8 \times 1/8$$
 (corners) + $6 \times 1/2$ (faces) = 4.

If the spheres have radii *r*, their volume is $\frac{4}{3}\pi r^3$ The total volume occupied is $\frac{16}{3}\pi r^3$.

The atoms touch along the diagonal of one of the faces so that the length of the diagonal is 4r. Using Pythagoras' theorem, the length of the side of the cube is:

$$a^2 + a^2 = (4r)^2$$
 or $a = \sqrt{8}r$



Hence the cube volume = $a^3 = (8)^{3/2} r^3$

The percentage of this which is occupied is therefore:

percentage occupied =
$$\frac{(16/3)\pi r^3}{(8)^{3/2}r^3} \times 100 = 74\%$$

(b) In a body centred cubic lattice, there are atoms on each corner and at the centre of the cube. The atoms on the corners are shared between 8 cells so 1/8 is located in this cell. The atoms in the centre is totally in this cube. The total number of atoms in the cell is therefore

$$8 \times 1/8$$
 (corners) + 1 (centre) = 2.

The spheres touch along the body diagonal.

A similar calculation to that in (a) gives the percentage occupied = 68%

(c) In a simple centred cubic lattice, there are only atoms on each corner. These atoms are shared between 8 cells so 1/8 is located in this cell.

8 × 1/8 (corners) = 1.

The spheres touch along the edges.



A similar calculation to that in (a) gives the percentage occupied = 52%

Note that the face centred cubic unit cell gives the highest percentage occupation – it is the only closed packed structure out of these three.

- 6. There are 12 nearest neighbours in a closed packed structure.
- 7. (a) The eight atoms on the corners are shared with eight other unit cells. The total number of this atom type in this unit cell is therefore $8 \times 1/8 = 1$.

The atom at the centre is only in this cube so the total number of this atom type is also 1.

The stoichiometry is 1:1 so the formula is XY

(b) If the atoms are touching along an edge and have radii = y, the cell edge has a length 2y. The length of the body diagonal, d, is given by:

$$d^{2} = (2y)^{2} + (2y)^{2} + (2y)^{2} = 12y^{2}$$
 so $d = 2\sqrt{3}y$

The body diagonal has a length of (y) + (2x) + (y) where x is the radius of atom X and 2x is the size of the hole. Thus, $x = (\sqrt{3} - 1)y$ or $2x = 2(\sqrt{3} - 1)y$. The atom at the centre can have a radius up to 73% that of the atoms at the corners.



7. CaSO₄(s) \rightleftharpoons Ca²⁺(aq) + SO₄²⁻(aq)

The molar mass of CaSO₄ is (40.08 (Ca) + 32.07 (S) + 4 × 16.00 (O)) g mol⁻¹ = 136.07 g mol⁻¹.

The solubility of 2.1 g L⁻¹ therefore corresponds to $\frac{2.1 \text{ g L}^{-1}}{136.07 \text{ g mol}^{-1}} = 0.015 \text{ mol L}^{-1}$.

As one mole of $Ca^{2+}(aq)$ and one mole of $SO_4^{2-}(aq)$ are produced from every mole of $CaSO_4$ which dissolves:

$$K_{\rm sp} = [{\rm Ca}^{2+}({\rm aq})][{\rm SO}_4^{2-}({\rm aq})] = 0.015 \times 0.015 = 2.4 \times 10^{-4}.$$

8. Mg(OH)₂(s) dissolves according to the equilibrium:

Mg(OH)₂(s)
$$\Longrightarrow$$
 Mg²⁺(aq) + 2OH-(aq) with $K_{sp} = [Mg^{2+}(aq)][OH(aq)]^2$

As pH + pOH = 14.00, pOH = (14.00 - 7.00) = 7.00 at pH = 7.00.

Hence, as $pOH = -log_{10}([OH-(aq)])$,

 $[OH-(aq)] = 10^{-7.00}$

As $K_{\rm sp}$ (Mg(OH)₂) = 7.1 × 10⁻¹²,

solubility =
$$[Mg^{2+}(aq)] = \frac{K_{sp}}{[OH^{-}(aq)]^{2}} = \frac{(7.1 \times 10^{-12})}{(10^{-7.00})^{2}} = 710 \text{ M}$$

The formula mass of Mg(OH)₂ is:

$$(24.31 \text{ (Mg)} + 16.00 \text{ (O)} + 1.008 \text{ (H)}) \text{ g mol}^{-1} = 58.326 \text{ g mol}^{-1}.$$

Thus, the mass of $Mg(OH)_2$ which will dissolve at pH = 7.00 is:

mass of Mg(OH)₂ = number of moles × formula mass = $(710 \text{ mol}) \times (58.326 \text{ g mol}^{-1}) = 41 \times 10^3 \text{ g} = 41 \text{ kg}.$

2.0 g of Mg(OH)₂ will easily dissolve.

Note that, although dissolution of $Mg(OH)_2$ produces OH- ions, the solution is buffered to keep [OH-(aq)] low. In a normal solution, the solubility of $Mg(OH)_2$ is *very* low as dissolution produces both $Mg^{2+}(aq)$ and OH-(aq) ions.