The IMFs (intermolecular forces) to consider can be divided into the following categories (see below).

(i) Ionic: Metal salts are often ionic in character. Metals form cations in compounds and combine with ions to make ionic compounds. When a compound is ionic, ionic forces (opposite charges attract) are the only types of IMFs present.

Covalently bonded compounds are formed by sharing one or more electron pairs between bonding atoms. Sharing leads to multiple types of IMFs, based on the nature of the bond and the type of sharing (equal or unequal, the latter forms polar bonds).

(ii) When electrons are shared equally (true covalent bond), only fleeting dipoles are created which rapidly switch between either atom in the bond, creating momentary dipoles that help hold molecules together. These are called London dispersion forces. Not all molecules with polar bonds are polar. When bond dipoles cancel, the end result is a nonpolar molecule and these are bonded together, once again by London dispersion forces.

(iii) When the presence of polar bonds results in the molecule being polar overall, the most predominant form of intermolecular attraction are the dipole-dipole forces. The molecule may also contain some true covalent bonds, and at these parts of the molecule the IMFs continue to be the London dispersion forces.

(iv) When ionic compounds are dissolved in water, they dissociate (does not matter whether dissociation is complete or incomplete). The ions formed in solution are attracted to the opposite poles of the water molecule (which is a polar compound) and these forces are referred to as ion-dipole attractions. (Note: Solids cannot have ion dipole attractions unless you have a homogenous mixture (like a melt) of an ionic and a polar compound.

(v) Hydrogen bonding can be exhibit by ceratin molecules. When a highly electronegative atom such as F, O or N is bonded to a hydrogen, a strong dipole is formed. This coupled with the lone pairs present on the N, O and F atoms has a tremendous potential for attracting the positive hydrogen in the dipole of the next molecule. Hydrogen bonds tend to be stronger forces than dipole dipole attractions between polar molecules, and explain the reason why water is a liquid at room temperature and has a rather high boiling point in comparison to several other, larger molecules.

Note that whenever molecules are formed by electron sharing between atoms, London forces will always be present, even though the primary attraction comes from dipole-dipole interactions in molecules that are polar. In many instances, Lewis structures have to be drawn that indicate the presence of lone pair(s) and affect the shape of the molecule. A summary of molecule types, shapes and polarities is given below:

<table>
<thead>
<tr>
<th>Type</th>
<th>Orientation</th>
<th>Hybridization</th>
<th>~ Angles</th>
<th>Shape</th>
<th>Polarity</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>AX₂</td>
<td>Linear</td>
<td>sp</td>
<td>180°</td>
<td>Linear</td>
<td>non-polar</td>
<td>CO₂</td>
</tr>
<tr>
<td>AX₃</td>
<td>Trigonal planar</td>
<td>sp₂</td>
<td>120°</td>
<td>Trigonal planar</td>
<td>non-polar</td>
<td>BF₃</td>
</tr>
<tr>
<td>AX₄</td>
<td>Tetrahedral</td>
<td>sp³</td>
<td>109.5°</td>
<td>Tetrahedral</td>
<td>non-polar</td>
<td>CH₄</td>
</tr>
<tr>
<td>AX₃E</td>
<td>Tetrahedral</td>
<td>sp³</td>
<td>109.5°</td>
<td>Trigonal pyramid</td>
<td>polar</td>
<td>NH₃</td>
</tr>
<tr>
<td>AX₂E₂</td>
<td>Tetrahedral</td>
<td>sp³</td>
<td>109.5°</td>
<td>Angular (bent)</td>
<td>polar</td>
<td>OH₂ (water)</td>
</tr>
<tr>
<td>AX₅</td>
<td>Trigonal bipyramid</td>
<td>dsp³ (sp³d)</td>
<td>90°, 120°, 180°</td>
<td>Trigonal bipyramid</td>
<td>non-polar</td>
<td>PCl₅</td>
</tr>
<tr>
<td>AX₄E</td>
<td>Trigonal bipyramid</td>
<td>dsp³</td>
<td>90°, 120°, 180°</td>
<td>See-saw</td>
<td>polar</td>
<td>SF₄</td>
</tr>
<tr>
<td>AX₃E₂</td>
<td>Trigonal bipyramid</td>
<td>dsp³</td>
<td>120° (approx)</td>
<td>T (or Y) shaped</td>
<td>polar</td>
<td>IF₃</td>
</tr>
<tr>
<td>AX₂E₃</td>
<td>Trigonal bipyramid</td>
<td>dsp³</td>
<td>--</td>
<td>Angular (bent)</td>
<td>polar</td>
<td>XeF₂</td>
</tr>
<tr>
<td>AX₆</td>
<td>Octahedral</td>
<td>d2sp³</td>
<td>90°, 180°</td>
<td>Octahedral</td>
<td>non-polar</td>
<td>SF₆</td>
</tr>
<tr>
<td>AX₅E</td>
<td>Octahedral</td>
<td>d2sp³</td>
<td>90°</td>
<td>Square pyramid</td>
<td>polar</td>
<td>ClF₅</td>
</tr>
<tr>
<td>AX₄E₂</td>
<td>Octahedral</td>
<td>d2sp³</td>
<td>90°</td>
<td>Square planar</td>
<td>non-polar</td>
<td>XeF₄</td>
</tr>
</tbody>
</table>
36. Identify the most important types of interparticle forces present in the solids of each of the following substances.

(a) NH4Cl: ionic compound, ionic forces
(b) Teflon, CF3(CF2CF2)nCF3: the molecule is that of a polymer, even though the C–F bonds are polar, the large size of the molecule makes the London dispersion forces the most predominant IMFs
(c) Polyethylene, CH3(CH2CH2)nCH3, the polymer molecule is comprised of covalent bonds, the molecule is large, London dispersion forces predominate.
(d) CHCl3, the shape of the molecule is tetrahedral, but there is one polar C–Cl bond, making the compound polar. Dipole-dipole forces are the most predominant, even though to a small extent, the C–H bonds also have London dispersion forces.
(e) NH3, the N–H bond is polar, the shape of the molecule is trigonal pyramidal due to the presence of the lone pair on N, the compound is polar. Dipole-dipole forces are the most predominant.
(f) NO, the N–O bond is polar, dipole-dipole forces predominate, although wherever electrons are shared London dispersion forces will always be present too.
(g) BF3, the molecule is trigonal planar, and nonpolar, only London dispersion forces predominate.

38. Rationalize the difference in boiling points for each of the following pairs of substances:

As a general rule of thumb, boiling points (or melting points for solids) increase as the molar mass of the molecule increases. The lower alkanes are all gases, then come the liquids. The higher alkanes are solids.

When hydrogen bonding or polarity is a property of the molecule, the IMFs generally increase in comparison to the nonpolar molecules. Thus, water is a liquid at room temperature (it is both polar and hydrogen bonded) but H2S (S is in the same group as O) is still a gas; CO2 and CS2 on the other hand, stick to the trend, CO2 is a gas, and CS2 is a liquid.

(a) n-pentane (CH3CH2CH2CH2CH3, 36.2ºC), neopentane (C(CH3)4, 9.5ºC): The neopentane molecule is more compact than the n-pentane molecule, leading to a larger surface area of contact in n-pentane. This increases the London forces between molecules of n-pentane leading to a higher boiling point.

(b) dimethyl ether (CH3OCH3, –25ºC), ethanol (CH3CH2OH, 79ºC): The –O–H bond in ethanol makes the molecule capable of hydrogen bonding. The –O–CH3 of dimethyl ether is incapable of doing that. Hydrogen bonding results in the molecules of ethanol being more tightly held than those of dimethyl ether, leading to a higher boiling point for ethanol.

(c) HF (20ºC), HCl (–85ºC); HF is capable of H bonding, HCl is not making HF a liquid despite its smaller molar mass.

(d) HCl (–85ºC), LiCl (1360ºC); LiCl is a solid held together by ionic bonding and ionic IMFs, the strongest of all, HCl is only held together by dipole dipole interactions and London dispersion forces.

(e) n-pentane (CH3CH2CH2CH2CH3, 36.2ºC), n-propane (CH3CH2CH3, –42ºC): n-propane is lower boiling due to its lower molar mass, both are polar molecules, both are straight chain, n-pentane has more surface area for London dispersion forces.

(f) n-propane (CH3CH2CH3, –42ºC), dimethyl ether (CH3OCH3, –25ºC): Dimethyl ether is a polar molecule, so there are two kinds of IMFs The dipole dipole attractions and London dispersion forces whereas n-propane has only London dispersion forces holding the molecules together.

40. In each of the following groups of substances, pick the one that has the given property. Justify each answer.

(a) the highest boiling point, CCl4, CF4, or CBr4; All molecules are non-polar, CBr4 is the largest with the most electrons and the strongest London dispersion forces.

(b) the lowest freezing point, LiF, Cl2, HBr; Cl2, ionic forces in LiF are very strong, HBr is a polar molecule, but Cl2 is only held together by London dispersion forces.

(c) the smallest vapor pressure at 25ºC: CH3OCH3, CH3CH2OH, CH3CH2CH3; vapor pressure at any
given temperature is related to the boiling point of a substance, read this as which of the above has the highest boiling point. Ethanol, CH₃CH₂OH has the highest boiling point due to H bonding and dipole-dipole forces in addition to London forces and the lowest vapor pressure (least volatile) of the lot.

(d) greatest viscosity H₂S, HF, H₂O₂; H–O–H has the highest viscosity, the structure produces the greatest amount of H bonding between molecules, which far exceeds that of HF. Long chains (several units) of H₂O₂ molecules can get tangled with each other leading to a greater viscosity.

(e) greatest heat of vaporization: H₂CO, CH₃CH₃, CH₄; H₂CO (methanal or formaldehyde) is a polar compound and the molecules are held together by stronger IMFs than the London dispersion forces of ethane and methane.

(f) smallest enthalpy of fusion: I₂, CsBr, CaO: Easiest to melt, I₂ has only London dispersion forces

42. Explain why water forms into beads on a waxed car finish.
Waxes are polymeric materials that are nonpolar and therefore can only interact with the neighboring molecules using London dispersion forces. Water molecules attract each other using H bonding, dipole-dipole attractions and London dispersion forces. Thus the potential that water molecules will be more strongly drawn to each other is very high, water pulls up and away from the surface of the wax, making a spherical bead with the smallest possible contact area. (The rule of thumb here is like attracts like, water beads on wax but spreads on glass, nonpolar liquids will spread on wax but will bead on a glass surface.

44. Carbon diselenide (CSe₂) is a liquid at room temperature. The normal boiling point is 125ºC, and the melting point is –45.5ºC. Carbon disulfide (CS₂) is also a liquid at room temperature with normal boiling and melting points of 46.5ºC and –111.6ºC, respectively. How do the strengths of the intermolecular forces vary from CO₂ to CS₂ to CSe₂? Explain.
CO₂ is a gas at room temperature whereas CS₂ is a liquid, and carbon diselenide is also a liquid. O, S and Se belong to the same group and have the same number of valence electrons, and form identical Lewis structures. All three molecules are linear and nonpolar. As the total number of electrons in the atom increases going down a group, stronger London dispersion forces can be exhibit by the larger atoms (and molecules). The strength of London forces increases in order of the increasing sizes of the molecules which is CO₂ < CS₂ < CSe₂.

46. X-rays of wavelength 2.63Å were used to analyze a crystal. The angle of first order diffraction (n = 1 in the Bragg equation) was 15.55 degrees. What is the spacing between the crystal planes, and what would be the angle for second order diffraction (n = 2)?
nλ = 2dsinθ; d = \frac{nλ}{2sinθ} = \frac{1 \times 2.63}{2 \times sin 15.55°} = 4.91 Å = 4.91 \times 10^{-10} m = 491 pm.
For second order diffraction:
\sin θ = \frac{nλ}{2d} = \frac{2 \times 2.63}{2 \times 4.91} = 0.536, θ = 32.4°

50. You are given a small bar of an unknown metal X. You find the density of the metal to be 10.5 g/cm³. An X-ray diffraction experiment measures the edge length of the face-centered cubic unit cell as 4.09 Å (1 Å = 10⁻¹⁰ m). Identify X.
The cubic cell is face-centered, there are 4 atoms per unit cell. The edge length = 4.09 \times 10⁻¹⁰ m = 4.09 \times 10⁻⁸ cm. The volume of the cell is (4.09 \times 10⁻⁸ cm)³ = 6.8417929 \times 10⁻²³ cm³.
Mass = Vol \times density = 6.8417929 \times 10⁻²³ cm³ \times 10.5 = 7.18388255 \times 10⁻²² g (mass of 4 atoms).
This can be converted to the molar mass by either of two methods:
Method 1: \frac{7.18388255 \times 10⁻²² g}{4 \text{ atoms}} \times \frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} = 108.1533518 g/mol, the metal is Ag (silver).
Method 2: moles of X = 4 \text{ atoms} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} = 6.64231152 \times 10^{-24} \text{ mol}

Molar mass of X = \frac{\text{mass (g)}}{\text{mol}} = \frac{7.18388255 \times 10^{-22} \text{ g}}{6.64231152 \times 10^{-24} \text{ mol}} = 108.1533518 \text{ g/mol}, \text{ the metal is Ag (silver)}.


\[ E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ Js} \times 2.9998 \times 10^8 \text{ m/s}}{730 \times 10^{-9} \text{ m}} = 2.72 \times 10^{-19} \text{ J} \]

66. The CsCl structure is a simple cubic array of chloride ions with a cesium ion at the center of each cubic array. Given that the density of cesium chloride is 3.97 \text{ g/cm}^3, and assuming that the chloride and cesium ions touch along the body diagonal of the cubic unit cell, calculate the distance between the centers of adjacent Cs\(^+\) and Cl\(^-\) ions in the solid. Compare this value with the expected distance based on the sizes of the ions. The ionic radius of Cs\(^+\) is 169 \text{ pm}, and the ionic radius of Cl\(^-\) is 181 \text{ pm}.

The arrangement of ions is that of a body centered cubic unit cell. The length of the body diagonal = 4r.

In this case \(2r(\text{Cs}^+) + 2r(\text{Cl}^-)\).

The unit cell contains 1 CsCl molecule (1 formula unit),

\[ \text{mass} = 1 \text{ CsCl formula unit} \times \frac{1 \text{ mol CsCl}}{6.022 \times 10^{23} \text{ formula units CsCl}} \times \frac{168.4 \text{ g CsCl}}{1 \text{ mol CsCl}} = 2.79641315 \times 10^{-22} \text{ g} \]

\[ \text{Volume} = \frac{\text{mass}}{\text{density}} = \frac{2.79641315 \times 10^{-22} \text{ g}}{3.97 \text{ g/cm}^3} = 7.04386184 \times 10^{-23} \text{ cm}^3 = l^3; \]

\(l = 4.129875344 \times 10^{-8} \text{ cm} = 413 \text{ pm} \).

Since the ions touch at the body diagonal:

\[ l\sqrt{3} = 2r(\text{Cs}^+) + 2r(\text{Cl}^-) = 413 \times \sqrt{3} = 715.3153924 \text{ pm}. \]

Distance between ion centers = \(r(\text{Cs}^+) + r(\text{Cl}^-)\) = \(715.3153924 \text{ pm}\) / 2 = 357.6576962 pm.

Distance between ion centers (based on ionic radii) = \(r(\text{Cs}^+) + r(\text{Cl}^-)\) = 350 pm.

The actual distance is about 8 pm greater than the value calculated on the basis of the ionic radii.

68. What type of solid will each of the following substances form?

(a) diamond: atomic, network
(b) PH\(_3\): molecular
(c) H\(_2\): molecular
(d) Mg: atomic, metallic
(e) KCl: ionic
(f) quartz: network
(g) NH\(_4\)NO\(_3\): ionic
(h) SF\(_2\): molecular
(i) Ar: atomic
(j) Cu: atomic, metallic
(k) C\(_6\)H\(_{12}\)O\(_6\): molecular

74. The structures of another class of ceramic, high temperature superconductors are shown in the fig. on p. 504.

* The problem mentions Tl (thallium) but the diagram shows Ti (titanium). Since Tl metal has an oxidation state of 3+, we will stick by Tl.
(a) Determine the formula of each of these four superconductors.
For structure (a):
Ba: 2 Ba inside unit cell = 2 atoms.
Tl: 8 corners x $\frac{1}{8}$ atom/corner = 1 atom.
Cu: 4 edges x $\frac{1}{4}$ atom/edge = 1 atom.
O: 6 faces x $\frac{1}{2}$ atom/face + 8 edges x $\frac{1}{4}$ atom/edge = 5 atoms; the formula is TlCuBa2O5

Using similar basis for calculating the number of atoms in each of structures (b), (c) and (d):
Structure (b): TlCu2Ba2CaO7
Structure (c): TlCu3Ba2Ca2O9 and
Structure (d): TlCu4Ba2Ca3O11.

(b) One of the structural features that appears to be essential for high temperature superconductivity is the presence of planar sheets of copper and oxygen atoms. As the number of sheets in each unit cell increases, the temperature for the onset of superconductivity increases. Order the four structures from the lowest to the highest superconducting temperature.

Planar sheets (in the same plane) of Cu and O exist in all structures; structure (a) has 1, (b) has 2, (c) has 3 and (d) has 4. According to this, the order of increasing superconductivity (lowest to highest) is (a) < (b) < (c) < (d).

(c) Assign oxidation states to Cu in each structure assuming Tl exists as Tl3+. The oxidation states of Ca, Ba and O are assumed to be +2, +2 and –2, respectively.
Assuming the given oxidation states, let Cu = x. Thus, for structure (a) TlCuBa2O5:

\[(+3) + (+x) + (+2 \times 2) + (−2 \times 5) = 0; \ x = +3; \ Cu \ exists \ as \ Cu^{3+}\]
Likewise: For structure (b): Cu is +5/2, since there are 2 Cu atoms, one must be +2 and the other +3.
For structure (c): Cu is +7/3; with three Cu atoms, it must be +2, +2, and +3.
For structure (d): Cu is +9/4; with four Cu atoms, the division works out as three +2 and one +3.

(d) It also appears that Cu must display a mixture of oxidation states for a material to exhibit superconductivity. Explain how this occurs in these materials as well as in the superconductor in Ex. 73.
The variable oxidation states of Cu are achieved by varying the numbers of Ca, Cu and O present in each unit cell. One of the options is also to omit certain atoms altogether, which is what can be seen with O atoms being omitted from various sites in the crystal lattice of the material in Ex 73.

76. From the following data for liquid nitric acid, determine the heat of vaporization and normal boiling point.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Temp (K)</th>
<th>1/T</th>
<th>Tvap (mm Hg)</th>
<th>ln Pvap</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.</td>
<td>273 K</td>
<td>3.66E–3</td>
<td>14.4</td>
<td>2.67</td>
</tr>
<tr>
<td>10.</td>
<td>283 K</td>
<td>3.53E–3</td>
<td>26.6</td>
<td>3.28</td>
</tr>
<tr>
<td>20.</td>
<td>293 K</td>
<td>3.41E–3</td>
<td>47.9</td>
<td>3.87</td>
</tr>
<tr>
<td>30.</td>
<td>303 K</td>
<td>3.30E–3</td>
<td>81.3</td>
<td>4.40</td>
</tr>
<tr>
<td>40.</td>
<td>313 K</td>
<td>3.19E–3</td>
<td>133</td>
<td>4.89</td>
</tr>
<tr>
<td>50.</td>
<td>323 K</td>
<td>3.10E–3</td>
<td>208</td>
<td>5.34</td>
</tr>
<tr>
<td>80.</td>
<td>353 K</td>
<td>2.83E–3</td>
<td>670.</td>
<td>6.51</td>
</tr>
</tbody>
</table>

Plot data of ln vapor pressure (Y axis) vs. 1/temperature (absolute T, X axis) and determine the equation in the form $y = mx + c$. Extrapolate to determine T when the vapor pressure is 760 mm Hg. The values to be plotted have been incorporated into table above.
The slope is $-\Delta Hvap/R$ ($R = \text{gas constant} = 8.3145 \text{ J/K-mol}$) = $-4600 \text{ K}$; solve $\Delta Hvap = 38 \text{ kJ/mol}$
The Clausius Clayperon equation can be used to determine the normal boiling point:
\[ \ln \left( \frac{P_1}{P_2} \right) = \frac{\Delta H}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \]; at the normal boiling point, pressure = 760 torr

\[ \ln \left( \frac{14.4}{760} \right) = \frac{38000}{8.3145} \frac{\text{J}}{\text{mol} \cdot \text{K}} \left( \frac{1}{T_2} - \frac{1}{273 \text{ K}} \right); T_2 = 357 \text{ K} (84^\circ \text{C}) \].

82. Given the data in Ex. 81 on substance X, calculate the energy that must be removed to convert substance X from a gas at 100.ºC to a solid at –50.ºC. Assume X has a molar mass of 75.0 g/mol.

The following is the data from Ex. 81

\( \Delta H_{\text{vap}} = 20. \text{ kJ/mol}; \Delta H_{\text{fus}} = 5.0 \text{ kJ/mol}; C(\text{s}) = 3.0 \text{ J/g-ºC}; C(\text{l}) = 2.5 \text{ J/g-ºC}; C(\text{g}) = 1.0 \text{ J/g-ºC}; \text{bp} = 75^\circ \text{C}, \text{mp} = 15^\circ \text{C}. \)

(a) The substance exists as a gas at 100.ºC and must be cooled to the condensation point 75ºC (bp), (b) the gas will then condense to the liquid at 75ºC (\( -\Delta H_{\text{vap}} = -20. \text{ kJ/mol} \)). (c) The liquid then needs to be cooled to its freezing point 15ºC. (d) Conversion to solid at this stage releases energy equal to the latent heat of fusion (freezing = – fusion). (e) Finally the solid is cooled to –50ºC. The sum of energies (a) through (e) is the total amount of heat that needs to be removed. (Since heat is being removed throughout, it will be indicated as “–” for substance X, we will forego the sign convention.)

Remember! Heats of fusion and vaporization (the opposite processes are freezing or conversion of liquid to solid and condensation or conversion of gas to liquid, respectively) are generally given in kJ/mol, do not forget to change the mass to mols and remember energy will be calculated in kJ. Heat capacity is generally given in J and is calculated per gram of the substance. When adding the energies, make sure they are in the same units!!!

The problem fails to mention the mass of substance X. Given that it has a molar mass of 75.0 g/mol, we will base all calculations for 1 mol of the substance first.

(a) Cooling of gas: \( q = m \times C(\text{g}) \times \Delta T = 75 \text{ g} \times 1.0 \frac{\text{J}}{\text{g-ºC}} \times (100 - 75)^\circ \text{C} = 1875 \text{ J} \)

(b) Condensation of gas to liquid = \( n \times \Delta H_{\text{vap}} = 1 \text{ mol} \times 20. \text{ kJ/mol} = 20000 \text{ J} \)

(c) Cooling of liquid: \( q = m \times C(\text{l}) \times \Delta T = 75 \text{ g} \times 2.5 \frac{\text{J}}{\text{g-ºC}} \times [75 - (-15)]^\circ \text{C} = 16875 \text{ J} \)

(d) Freezing of liquid to solid: \( n \times \Delta H_{\text{fus}} = 1 \text{ mol} \times 5.0 \text{ kJ/mol} = 5.0 \text{ kJ} = 5000 \text{ J} \)

(e) Cooling of solid: \( q = m \times C(\text{s}) \times \Delta T = 75 \text{ g} \times 3.0 \frac{\text{J}}{\text{g-ºC}} \times [-15 - (-50)]^\circ \text{C} = 7875 \text{ J} \)

Thus, the total energy removed:

1875 J + 20000 J + 16875 J + 5000 J + 7875 J = 51625 J = 51.625 kJ of energy must be removed per mole of substance X to convert it from a gas at 100ºC to a solid at –50ºC.

Suppose a mass of X had been mentioned. See problem 84 below on the use of mass in g and amount in mol to be used in different parts of the calculation.

84. Consider a 75.0 g sample of \( \text{H}_2\text{O}(g) \) at 125ºC. What phase or phases are present when 215 kJ of energy is removed from this sample?

The heat capacity of \( \text{H}_2\text{O}(g) \) is: \( C(\text{s}) = 2.1 \text{ J/g-ºC}; C(\text{l}) = 4.2 \text{ J/g-ºC}; C(\text{g}) = 2.0 \text{ J/g-ºC}; \Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}; \Delta H_{\text{fus}} = 6.02 \text{ kJ/mol} \)

The same steps as in problem 82, except this time a fixed amount of energy is being removed, it will have to be determined how much this energy will accomplish.
75.0 g H₂O \times \frac{1 \text{ mol H}_2\text{O}}{18.016 \text{ g H}_2\text{O}} = 4.162966252 \text{ mol H}_2\text{O}

Amount of energy removed = 215 kJ = 215000 J

(a) From 125°C, the gas cools to 100°C: 
\[ q = m \times C(g) \times \Delta T = 75. \text{ g} \times 2.0 \frac{J}{\text{g} \cdot ^\circ \text{C}} \times [125 - 100] \] = 3750 J = 3.750 kJ

(b) Condensation of gas to liquid: 
\[ n \times \Delta H_{vap} = 4.162966252 \text{ mol H}_2\text{O} \times 40.7 \text{ kJ/mol} = 169.4327265 \text{ kJ} = 169432.7265 \text{ J} \]

(c) Cooling of liquid: 
\[ q = m \times C(l) \times \Delta T = 75. \text{ g} \times 4.2 \frac{J}{\text{g} \cdot ^\circ \text{C}} \times (100 - 0) \] = 31500 J = 31.500 kJ

Keep an eye on the numbers, so far we have removed: 3.750 + 169.433 + 31.500 kJ = 204.683 kJ of energy.

Remaining energy = 215 – 204.683 = 10.317 kJ

We have 4+ moles of water and at 6.02 kJ/mol, it will take more than 24 kJ of energy to convert the entire water to ice. That much energy is not available. Hence ice and water will remain in equilibrium.

For the more discerning, the amount of water that can be converted to ice:
\[ n \times 6.02 = 10.317; \quad n = 1.713787375 \text{ moles of water} \times 18.016 \text{ g/mol} = 30.8759336 \text{ g of water} \] will be converted to ice, the remainder will remain in equilibrium with the ice as a liquid. The final temperature of the sample is 0°C, the temperature at which ice and water remain in equilibrium.

86. A 0.250 g chunk of sodium metal is cautiously dropped into a mixture of 50.0 g of water and 50.0 g of ice, both at 0°C. The reaction is: 2Na(s) + 2H₂O(l) → 2NaOH(aq) + H₂(g); \( \Delta H = -368 \text{ kJ} \) Will the ice melt? Assuming the final mixture has a specific heat capacity of 4.18 J/g-°C, calculate the final temperature. The enthalpy of fusion for ice is 6.02 kJ/mol.

The total mass of water is 100.0 g.

The reaction enthalpy is \(-368 \text{ kJ/mol}\), since 2 mol of sodium have reacted according to the balanced equation: the enthalpy change can be correlated to mol of sodium reacted: \(-368/2 = -184 \text{ kJ/mol of sodium reacted}\).

Amount of sodium reacted = 0.250 g \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} = 0.0108742932 \text{ mol Na}

Amount of energy released = 0.0108742932 \text{ mol Na} \times \frac{184 \text{ kJ}}{1 \text{ mol Na}} = 2.000869943 \text{ kJ} = 2000 \text{ J}

50.0 g of ice is 2.775 mol of ice, at 6.02 kJ/mol it will take much more than 2 kJ to melt all the ice present, ice still remains in the mixture, the final temperature remains at 0°C.

88. Sulfur exhibits two solid phases, rhombic and monoclinic. Use the accompanying phase diagram for sulfur to answer the following questions (the phase diagram is not to scale).

(a) How many triple points are in the phase diagram?

Three triple points.

(b) What phases are in equilibrium at each of the triple points?

At 95.31°C: rhombic, monoclinic, gas
At 115.18°C: monoclinic, liquid, gas.
At 153°C: rhombic, monoclinic, liquid.

(c) What is the stable phase at 1 atm and 100°C?

monoclinic solid phase.

(d) What are the normal melting point and the normal boiling point of sulfur?

115.21°C and 444.6°C, respectively.

(e) Which is the densest phase?
rhombic sulfur

(f) At a pressure of $1.0 \times 10^{-5}$ atm, can rhombic sulfur sublime?
No, the rhombic and gas phases are never at equilibrium under this condition, but monoclinic sulfur can sublime.

(g) What phase changes occur when the pressure on a sample of sulfur at 100°C is increased from $1.0 \times 10^{-8}$ atm to 1500 atm?
Assuming no change in temperature, the sample starts as a gas and converts to monoclinic sulfur, and finally to rhombic sulfur.

90. Like most substances, bromine exists in one of the three typical phases. Br$_2$ has a normal melting point of –7.2°C and a normal boiling point of 59°C. The triple point for Br$_2$ is –7.3°C and 40 Torr, and the critical point is 320°C and 100 atm. Using this information sketch a phase diagram for bromine indicating the points described above. Based on your phase diagram, order the three phases from least dense to most dense. What is the stable phase of Br$_2$ at room temperature and 1 atm? Under what temperature conditions can liquid bromine never exist? What phase changes occur as the temperature of a sample of bromine at 0.10 atm is increased from –50°C to 200°C?

![Phase Diagram for Bromine](image)

Since the triple point of bromine is lower than the freezing (melting) point, the slope of the solid liquid line is positive and solid Br$_2$ is more dense than the liquid phase. The gas phase is the least dense. The most stable phase at room temperature (~25°C) and 1 atm is the liquid phase. Liquid bromine can never exist at temperatures and pressures below the triple point and temperatures and pressures beyond the critical point. Since 40 torr = 0.053 atm, bromine is a solid at 0.10 atm and –50°C. As the temperature is increased to 200°C, the solid sublimes directly to the gas phase (assuming the pressure is kept constant).