

AP CHEMISTRY

IMFs and Condensed States of Matter

2016 EDITION

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		30 Zn 65.39	48 Cd 112.41	80 Hg 200.59	112 § (277)
		29 Cu 63.55	47 Ag 107.87	79 Au 196.97	111 § (272)
		28 Ni 58.69	46 Pd 106.42	78 Pt 195.08	110 § (269)
		27 Co 58.93	45 Rh 102.91	77 Ir 192.2	109 Mt (266)
		26 Fe 55.85	44 Ru 101.1	76 Os 190.2	108 Hs (265)
		25 Mn 54.938	43 Tc (98)	75 Re 186.21	107 Bh (262)
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	*Lanthanide Series:			†Actinide Series:	

2016 AP Chemistry - Intermolecular Forces

AP Chemistry Equations & Constants

Throughout the test the following symbols have the definitions specified unless otherwise noted.

U	2 7	1
	L, mL = liter(s), milliliter(s) g = gram(s)	mm Hg = millimeters of mercury J, kJ = joule(s), kilojoule(s)
	nm = nanometer(s)	V = volt(s)
	atm = atmosphere(s)	mol = mole(s)
ATOMIC S	TRUCTURE	
E = hv		E = energy
$c = \lambda v$		$\nu = \text{frequency}$
$c = \pi v$		λ = wavelength
		Planck's constant, $h = 6.626 \times 10^{-34} \text{ J s}$
		Speed of light, $c = 2.998 \times 10^8 \text{ m s}^{-1}$
		Avogadro's number = $6.022 \times 10^{23} \text{ mol}^{-1}$
		-
		Electron charge, $e = -1.602 \times 10^{-19}$ coulomb
EQUILIBR	IUM	
$K_c = \frac{1}{[A]}$	$\frac{c[D]^d}{a[B]^b}$, where $a + b B \rightleftharpoons c C + d D$	Equilibrium Constants
(P-	$(1)^{c}(P_{-})^{d}$	K_c (molar concentrations)
$K_p = \frac{(P_C)}{(P_A)}$	$\frac{\partial^{a}(B)}{\partial^{a}(B)}$	K_p (gas pressures)
- 1		K_a (weak acid)
$K_a = \frac{[\mathrm{H}^4]}{[\mathrm{I}^4]}$		K_b (weak base)
L.		K_w (water)
$K_b = \frac{[OI]}{}$	<u>1⁻][HB⁺]</u> [B]	
K = [H]	$[OH^{-}] = 1.0 \times 10^{-14} \text{ at } 25^{\circ}\text{C}$	
$= K_a$		
	p^{ν} og[H ⁺], pOH = $-\log[OH^{-}]$	
14 = pH		
- -	^ ^	
pH = pK	$a + \log \frac{[A^-]}{[HA]}$	
$pK_a = -1e$	$\log K_a$, $pK_b = -\log K_b$	
KINETICS		
$\ln[A]_t -$	$\ln[A]_0 = -kt$	k = rate constant
1	1	t = time
$\frac{1}{[\mathbf{A}]_t} - \frac{1}{[\mathbf{A}]_0} = kt$		
- •		$t_{1/2} = \text{half-life}$
	$t_{1/2} = \frac{0.693}{k}$	
	ñ	

2016 AP Chemistry Intermolecular Forces

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles } A}{\text{total moles}}$$

$$P_{total} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^{\circ}C + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

$$Molarity, M = \text{moles of solute per liter of solution}$$

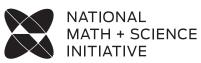
$$A = abc$$

P = pressureV =volume T = temperaturen = number of moles m = massM = molar massD = densityKE = kinetic energy v = velocity A = absorbancea = molar absorptivityb = path lengthc = concentrationGas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ $= 0.08206 \text{ L} \text{ atm mol}^{-1} \text{ K}^{-1}$ $= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$ 1 atm = 760 mm Hg= 760 torrSTP = 0.00 °C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$q = mc\Delta T$
$\Delta S^{\circ} = \sum S^{\circ}$ products $-\sum S^{\circ}$ reactants
$\Delta H^{\circ} = \sum \Delta H_f^{\circ} \text{ products } -\sum \Delta H_f^{\circ} \text{ reactants}$
$\Delta G^{\circ} = \sum \Delta G_f^{\circ}$ products $-\sum \Delta G_f^{\circ}$ reactants
$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ}$
$= -RT \ln K$
$= -n F E^{\circ}$
$I = \frac{q}{t}$

q = heat m = mass c = specific heat capacity T = temperature $S^{\circ} = standard entropy$ $H^{\circ} = standard enthalpy$ $G^{\circ} = standard free energy$ n = number of moles $E^{\circ} = standard reduction potential$ I = current (amperes) q = charge (coulombs) t = time (seconds)Faraday's constant, F = 96,485 coulombs per mole of electrons $1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$



2016 AP Chemistry - Intermolecular Forces

Intermolecular Forces

Solids, Liquids, Solutions, and Phase Changes

What I Absolutely Have to Know to Survive the AP* Exam

The following might indicate that the question deals with intermolecular forces: Boiling points; vapor pressure; melting points; network solid; crystalline solids; metallic solids; sea of electrons; delocalized electrons; triple point; sublimation; deposition; condensation; boiling; melting; freezing; intermolecular forces; vapor pressure; Coulombic interactions, etc...

Coulombic Interactions – It's All About the Attractions

The strength and nature of the electrostatic forces or Coulombic interactions that exist *between* particles explain the properties or behaviors of substances.

- When a substance undergoes a physical change the forces being overcome (the intermolecular interactions) are Coulombic in nature.
- When answering questions about the physical changes and properties of ionic solids always consider Coulomb's law it is all about the charge and the distance the charges are apart.

 $U_E \propto \frac{q^+ q^-}{d}$

Properties of Matter – Let's Get Physical

The different properties can be explained by differences in their structures at the particulate level. These properties reflect:

- Relative orderliness of the arrangement of their particles; i.e. the spacing between their (atoms, molecules, ions)
- Their relative freedom of motion
- Nature and strength of the interactions between them

SOLIDS	 Can be crystalline, where the particles are arranged in a regular 3-D structure, or they can be amorphous, where the particles do not have a regular, orderly arrangement. Motion of the individual particles is limited They do not undergo any overall translation with respect to each other. Inter-particle interactions provide the main criteria for the structures of solids
LIQUIDS	 Particles in liquids are very close to each other, and they are continually moving and colliding. Their particles are able to undergo translation with respect to each other and their arrangement Movement is influenced by the nature and strength of the inter-particle interactions that are present
NOTE	The solid and liquid phases for a particular substance generally have relatively small differences in molar volume. In both cases their particles are very close to each other at all times. This not true for the gas phase – where we assume the particles move independently having neither a definite shape or volume – as their particles are not "bound together" by inter-particle attractions

So.... What are these so called inter-particle attractions..?

	Interparticle Attraction	s – They're Sticky!
trends in can play •	a very important role in determining the overall	pecific structure and size of the particles involved strength of a particular intermolecular interaction. crucial biological structures are determined by the reflection of the presence of intermolecular
NOTE	<i>An interparticle attraction or intermolecular</i> <i>particles.</i>	force (IMF) is an attraction that occurs BETWEEN
	-	TRAparticle attractions or INTRAmolecular forces.
Without <i>ideally</i>	t these forces there would be no liquids or solids -	- everything would be in the gas phase, behaving
NOTE	 of IMFs Be on the look out for questions asking etc These particles have to overcome whate 	e changes you need to explain your response in terms about melting points, vapor pressure, boiling points, ever stickiness is holding them together – i.e. there
London	must be enough energy added to accom dispersion forces	plish this
•	Exist between all atoms and molecules Often are the strongest net IMF between large molecules ONLY IMF that for non-polar molecules	London dispersion forces
•	In the example on the right six particles are shown in a form depicting the symmetric distribution of electron density. In the second group of six, some of the particles have formed instantaneous dipoles.	
•	The instantaneous dipoles result from an unequal distribution of electrons. One particle with an instantaneous dipole will affect other particles adjacent to it producing a short-range attractive interaction. The larger the particle, the more electrons, the more polarizable its electron cloud, the stronger the force of attraction, the stronger the <i>London</i> <i>Dispersion forces</i> .	δ+ δ- δ+ δ- () () () ()

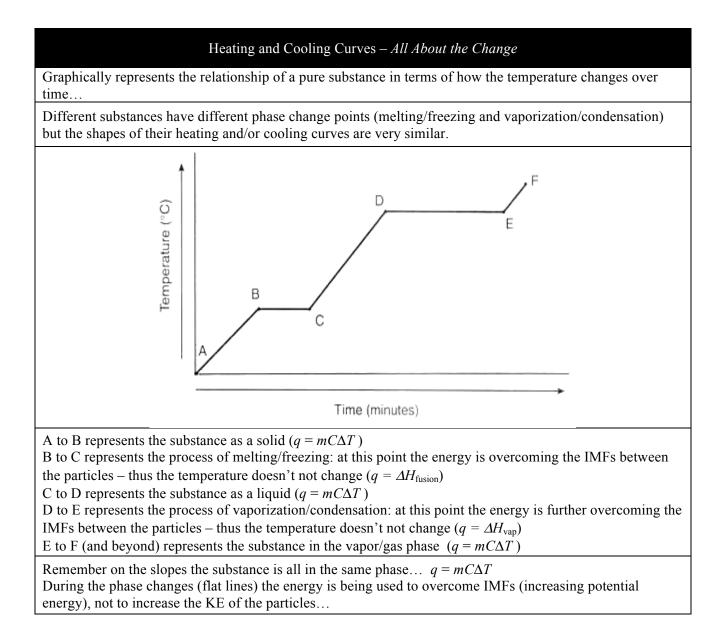
	Interparticle Attractions – 7	They're Sticky! con't.		
 D² th m Tl op at Th di In th Th 	bole interactions ipole forces result from the attraction among e positive ends and negative ends of polar olecules. The molecules align themselves such that the posite poles align – they maximize the traction and minimize the repulsion these dipoles result from the unequal stribution of electron density in the molecule termolecular dipole-dipole forces are weaker an ionic forces or covalent bonds. The larger the dipoles, the stronger the force of traction between the two molecules, the			
	ronger the <i>Dipole-Dipole force</i>			
 Dibe Dibe The mean of the m	<u>duced dipole interactions</u> ipole-induced dipole interactions are present etween a polar and nonpolar molecule. the strength of these forces increases with the agnitude of the dipole of the polar molecule ad with the polarizability of the nonpolar olecule <u>binding forces</u> (hydrogen bonding) yee of dipole force ydrogen bonding is a relatively strong type intermolecular interaction xists when hydrogen atoms that are ovalently bonded to the highly ectronegative atoms (N, O, and F) are also tracted to the negative end of a dipole formed y the electronegative atom (N, O, and F) in a <i>ifferent</i> molecule, or a <i>different part</i> of the me molecule (think about the complex ructures of a large biomolecule – like DNA) When hydrogen bonding is present, even small olecules may have strong intermolecular tractions. Think H ₂ O	hydrogen-bonding forces		
NOTE:	NOTE: Ionic interactions with dipoles are important in the solubility of ionic compounds in polar solvents. The positive and negative ions interact with the positive and negative ends of polar molecules, creating strong interactions – helping explain why NaCl is soluble in water.			
WATCH OUT!				

Solids – It's All About their Types			
Molecular Solids	 Composed of distinct, individual units of covalently bonded molecules attracted to each other through relatively weak intermolecular forces. Molecular solids: Are not expected to conduct electricity because their electrons are tightly held within the covalent bonds of each constituent molecule. Generally have a low melting point because of the relatively weak intermolecular forces present between the molecules. Sometimes composed of very large molecules, or polymers, with important commercial and biological applications. The solid contains arrangements of atoms or molecules that are organized in an orderly three-dimensional pattern 		
Covalent Network Solids	 Consist of atoms that are covalently bonded together into a 2-dimensional or 3-dimensional network. Are only formed from nonmetals: elemental (diamond, graphite, silicon) or two nonmetals (silicon dioxide and silicon carbide). The properties of covalent network solids are a reflection of their structure. Covalent network solids have high melting points because all of the atoms are covalently bonded. Three-dimensional covalent networks tend to be rigid and hard because the covalent bond angles are fixed. Generally, covalent network solids form in the carbon group because of their ability to form four covalent bonds. Carbon forms diamond and graphite Silicon forms a three-dimensional network similar in geometry to a diamond. Silicon's conductivity increases as temperature increases. 		
Metallic Solids	 Are good conductors of heat and electricity, have a wide range of melting points, and are shiny, malleable, ductile, and readily alloyed. Represented as positive kernels (or cores) consisting of the nucleus and inner electrons of each atom surrounded by a sea of mobile valence electrons. Metals are good conductors because the electrons are delocalized and relatively free to move. Metals are malleable and ductile because deforming the solid does not change the environment immediately surrounding each metal core. Metallic solids are often pure substances, but may also be mixtures called alloys. 		

	Solids – It's All About their Types con't
Ionic Solids	 Properties are related to the strong Coulombic interactions of positive and negative ions arranged in a regular three- dimensional array. Generally have low vapor pressure Tend to be brittle due to the repulsion of like charges caused when one layer slides across another layer. Their solids do not conduct electricity. However, when ionic solids are melted, they do conduct electricity because the ions are free to move. When ionic solids are dissolved in water, the separated ions are free to move; therefore, these solutions will conduct electricity. The attractive force between any two ions is governed by Coulomb's law: U_E ∝ q⁺q⁻/d For ions of a given charge, the smaller the ions, and thus the smaller the distance between ion centers, the stronger the Coulombic force of attraction, and the higher the melting point. Ions with higher charges lead to higher Coulombic forces, and therefore higher melting points.

	Liquids - All About their Properties
Surface Tension	Molecules in the interior of a liquid are attracted by surrounding molecules in all 3– dimensions. A molecule at the surface of a liquid is attracted only by the molecules below it and on each side of it. This leads to surface tension. High surface tension indicates strong IMFs.
Capillary Action	Described by spontaneous rising of a liquid in a narrow tube. Adhesive forces between the molecules and the glass overcome the forces (IMFs) between molecules themselves. Water has a higher attraction for glass than for itself so its meniscus is inverted or concave, while Hg has a higher attraction for other Hg atoms, thus its meniscus is convex.
Boiling Point	Boiling point is the temperature at which the vapor pressure of a liquid equals the atmospheric pressure; at this point the molecules have enough energy to overcome their IMFs and enter the vapor phase. At this temperature the substance exists in equilibrium as liquid and gas particles.
Vapor Pressure	 Vapor pressure is the pressure resulting from particles of a substance, which exist in the gas phase above the liquid (or solid). The weaker the IMFs, the higher the vapor pressure. <i>Why?</i> The substance can more easily overcome those IMFs and break away into the gas phase, increasing the number of molecules in the gas phase (at that temperature), thus increasing the pressure above the liquid. Increasing the temperature on the substance will increase the vapor pressure; again due to more molecules being able to overcome their IMFs and move into the gas phase.

Intermolecular Forces



Solution Formation – All About those IMFs		
Solutions are homogenous mixtures in which the physical properties are dependent on the concentration of		
the solute and the strengths of all interactions among the particles of the solutes and solvent.		
Substances with similar intermolecular interactions tend to be miscible or soluble in one another.		
 Solutions come in the form of solids, liquids, and gases For liquid solutions, the solute may be a gas, a liquid, or a solid. 		
Liquid solutions exhibit several general properties:		
 The components cannot be separated using filter paper. There are no components large enough to content visible light 		
 There are no components large enough to scatter visible light. The components can be separated using processes that are a result of the intermolecular interactions 		
between and among the components.		
 Chromatography (paper and column) separates chemical species by taking advantage of the differential strength of intermolecular interactions between and among the components. Distillation is used to separate chemical species by taking advantage of the differential strength of intermolecular interactions between and among the components and the effects these interactions have on the vapor pressures of the components in the mixture. 		
• The formation of a solution may be an exothermic or endothermic process, depending on the relative strengths of intermolecular/inter-particle interactions before and after the dissolution process.		
CAUTION Never use "like dissolves like" on the AP exam. EXPLAIN in terms of IMFs and energy		
Particles exhibit a number of inter-particle interactions (London dispersion, hydrogen binding, dipole-dipole, ion-dipole, etc) and it is these interactions that either PROMOTE or PREVENT solution formation. In order to dissolve a substance must Overcome (requires energy) <i>both</i> solute-solute and solvent-solvent interactions Form solute-solvent interactions upon mixing (releases energy)		
A solution WILL form when the energy released due to the solute-solvent interactions is the same as (or more than) the energy needed overcome the solute-solute and the solvent-solvent interactions. Example: dissolving acetone in chloroform		
H ₃ C CH ₃ H		
acetone and chloroform		
Solute-Solute: acetone forms dipole-dipole interactions between their particles Solvent-Solvent: chloroform forms dipole-dipole interactions between their particles Solute-Solvent: when mixed together dipole-dipole interactions form between the acetone and chloroform particles		
Example: dissolving sodium chloride in water		
H ^O H		
Na^+ and Cl^- and $water$		
Solute-Solute: positive sodium and negative chloride ions form ionic interactions between their particles Solvent-Solvent: water forms hydrogen binding interactions between their particles Solute-Solvent: when mixed together ion-dipole interactions form between the positive and negative ions of the salt and the polar water particles		

Solution Formation – All About those IMFs con't

A solution MAY or MAY NOT form when the energy released due to the solute-solvent interactions is less than the energy needed overcome the solute-solute and the solvent-solvent interactions. Whether the solution forms or not depends on the disparity between the two.

Example: dissolving hexane in water

 $CH_3-CH_2-CH_2-CH_2-CH_3 +$ hexane and

• Solute-Solute: hexane molecules form London dispersion interactions between their particles

water

- Solvent-Solvent: water forms hydrogen binding interactions between their particles
- Solute-Solvent: when mixed together polar water molecules can only interact with the non-polar hexane mlecules through London dispersion forces

Thus a solution does NOT form.

Although the tendency to mix is strong (increased entropy) the large energy disparity between overcoming the hydrogen binding forces in water and the relatively small energy gain from forming weak interactions between water and hexane is too large.

IMPORTANT

Melting points, vapor pressure, boiling points (really all phase change processes) are all about the strength of the intermolecular attractive forces. The physical change that accompanies any of these processes will require particles to overcome the attractive forces holding them together.

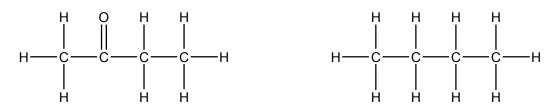
REMEMBER: If you are asked to compare 2 substances (higher boiling point, lower vapor pressure, which melts first, etc...) it's Coulombic! Write about Coulomb's Law for ionic substances and IMFs for molecular compounds

Connections to Other Chapters		
Periodicity	Bonding	
	Lewis Structures and Geometry	

NMSI SUPER PROBLEM

Answer the following questions using your knowledge of intermolecular forces and molecular structure. Your response <u>must</u> include specific information about <u>all</u> substances in each question.

A. The structures for butanone, CH₃COCH₂CH₃, and *n*-butane, CH₃CH₂CH₂CH₃, are shown below.



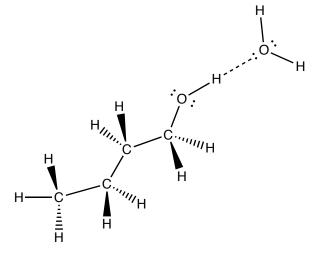
Identify the type of intermolecular forces in

(i) Butanone

(ii) *n*-butane

B. Butanone is much more soluble in H₂O than is *n*-butane. Account for this difference.

C. The substance *n*-butanol (CH₃CH₂CH₂CH₂OH) is shown below forming a hydrogen bond with a water molecule, as represented with a dashed line. There are 2 more locations where a water molecule would hydrogen bond with *n*-butanol. Draw both water molecules in their correct orientation where they would hydrogen bond with the *n*-butanol molecule.



D. Predict whether the enthalpy of vaporization, $\Delta H^{\circ}{}_{vap}$, for *n*-butanol will be greater than 32.2 kJ mol⁻¹; less than 21.0 kJ mol⁻¹; or between 21.0 kJ mol⁻¹ and 32.2 kJ mol⁻¹. Explain

Substance	$\Delta H^{\circ}_{vap} (\text{kJ mol}^{-1})$
<i>n</i> -butane ($CH_3CH_2CH_2CH_3$)	21.0
Butanone (CH ₃ COCH ₂ CH ₃)	32.2
<i>n</i> -butanol (CH ₃ CH ₂ CH ₂ CH ₂ OH)	?

E. Consider the three chloride compounds and the information in the table below.

Substance	Melting Point
PCl ₃	– 93.9°C
KC1	776°C
NaCl	801°C

Account for the difference in melting points.

The table below provides information about three of the noble gases.

Substance	Boiling Point (K)	Solubility in Water $(cm^3 kg^{-1})$
Ne	27.3	10.5
Ar	?	?
Xe	166.6	108.1

- F. Neon has a much lower boiling point than xenon. Explain.
- G. Xenon is much more soluble in water than neon. Explain
- H. Would argon's solubility in water be greater than or less than that of xenon?
- I. Give samples of liquid argon and liquid xenon in separate, identical, closed containers at the same temperature which would have the greatest vapor pressure?

AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS Modified for a Short Response

Use appropriate chemical principles to account for each of the following observations. In each part, your response <u>must</u> include specific information about <u>both</u> substances.

- (a) At 25°C and 1 atm, F_2 is a gas, whereas I_2 is a solid.
- (b) Ammonia, NH3, is very soluble in water, whereas phosphine, PH3, is only moderately soluble in water.

AP® CHEMISTRY FREE-RESPONSE QUESTIONS

Account for each of the following observations about pairs of substances. In your answers, use appropriate principles of chemical bonding and/or intermolecular forces. In each part, your answer must include references to <u>both</u> substances.

- (a) Even though NH₃ and CH₄ have similar molecular masses, NH₃ has a much higher normal boiling point $(-33^{\circ}C)$ than CH₄ $(-164^{\circ}C)$.
- (b) At 25°C and 1.0 atm, ethane (C_2H_6) is a gas and hexane (C_6H_{14}) is a liquid.
- (c) Si melts at a much higher temperature $(1,410^{\circ}C)$ than Cl₂ (-101°C).
- (d) MgO melts at a much higher temperature (2,852°C) than NaF (993°C).

2016 AP Chemistry - Intermolecular Forces **AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS**

Modified for a Short Response

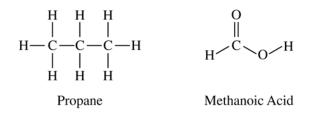
Use the information in the following table to answer the questions below.

Name	Lewis Electron-Dot Diagram	Boiling Point (°C)	Vapor Pressure at 20°C (mm Hg)
Dichloromethane	н :Сі:С:Н :Сі:	39.6	353
Carbon tetrachloride	:Ċl: :Ċl:Ċ:Ċl: :Ċl:	76.7	89

- (a) Dichloromethane has a greater solubility in water than carbon tetrachloride has. Account for this observation in terms of the intermolecular forces between <u>each</u> of the solutes and water.
- (b) In terms of intermolecular forces, explain why dichloromethane has a higher vapor pressure than carbon tetrachloride.

AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS Modified for a Short Response

Use principles of atomic structure, bonding, and intermolecular forces to answer the following questions. Your responses <u>must</u> include specific information about <u>all</u> substances referred to in each part.



(a) The complete structural formulas of propane, C_3H_8 , and methanoic acid, HCOOH, are shown above. In the table below, write the type(s) of intermolecular attractive force(s) that occur in each substance.

Substance	Boiling Point	Intermolecular Attractive Force(s)
Propane	229 K	
Methanoic acid	374 K	

(b) Use principles of intermolecular attractive forces to explain why methanoic acid has a higher boiling point than propane.