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[TP] Recall that the greater the electronegativity difference, the greater the polarity. The correct order of polarity of HBr, HCl and HI is (least to most) ...

- 0% 1. HBr < HCl < HI
- 0% 2. HBr < HI < HCl
- 0% 3. HCl < HBr < HI
- 0% 4. HCl < HI < HBr
- 0% 5. HI < HCl < HBr
- 100% 6. HI < HBr < HCl

001595

9 of 15

1 0

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1

Lecture 7 CH131 Summer 1 2021

Friday, June 4, 2021

Ch10: Solids, liquids and phase transitions

- Physical properties reflect intermolecular forces (IMF)
- Three kinds of IMF: London, H-bond, dipole-dipole
- London IMF dominate dipole-dipole IMF

Next: H-bonding IMF dominate London IMF; Practice: Boiling points and enthalpy of vaporization; Summary: Three kinds of IMF: London, H-bond, dipole-dipole; Units of pressure; Vapor pressure: Liquid-vapor equilibrium; Vapor pressure and boiling point; Phase diagrams; Ch11: Solutions

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2

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Physical properties reflect intermolecular forces

Melting and boiling reflect the forces between the particles of a substance.

Differences in these properties are due to differences in the relative strength of these forces.

Boiling requires particles to completely overcome the forces between them.

9

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Physical properties reflect intermolecular forces

Table 15-3 shows examples of differences in boiling points.

Compound	Chemical formula	Melting point/K	Boiling point/K	$\Delta H_{\text{vap}} / \text{kJ mol}^{-1}$	$\Delta H_{\text{fus}} / \text{kJ mol}^{-1}$
ammonia	NH ₃	195.42	239.82	5.66	23.33
argon	Ar	84			
bromine	Br				
neon	Ne	24.54	27.07	0.328	1.71
nitrogen	N ₂	63	77.36	0.71	5.57
oxygen	O ₂	54.36	90.20	0.44	6.82
sulfur dioxide	SO ₂	198	263.10	7.4	24.94
water	H ₂ O	273.15	373.15	6.01	40.65
xenon	Xe	161.36	165.04	2.27	12.57

10

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10

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Physical properties reflect intermolecular forces

Table 15-3 shows examples of differences in boiling points.

Why is Xe > Ne?

TABLE 15.3 Normal melting points, boiling points, and molar enthalpies of vaporization and fusion at these temperatures and one atm (1.01325 bar) pressure

Compound	Chemical formula	Melting point/K	Boiling point/K	ΔH_{fus} /kJ mol ⁻¹	ΔH_{vap} /kJ mol ⁻¹
ammonia	NH ₃	195.42	239.82	5.66	23.33
argon	Ar	83.8	87.3	1.2	6.5
bromine	Br ₂	265.9	331.9	10.57	30.91
neon	Ne	24.54	27.07	0.328	1.71
nitrogen	N ₂	63	77.36	0.71	5.57
oxygen	O ₂	54.36	90.20	0.44	6.82
sulfur dioxide	SO ₂	198	263.10	7.4	24.94
water	H ₂ O	273.15	373.15	6.01	40.65
xenon	Xe	161.36	165.04	2.27	12.57

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11

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Physical properties reflect intermolecular forces

Table 15-3 shows examples of differences in boiling points.

Why is O₂ > N₂?

TABLE 15.3 Normal melting points, boiling points, and molar enthalpies of vaporization and fusion at these temperatures and one atm (1.01325 bar) pressure

Compound	Chemical formula	Melting point/K	Boiling point/K	ΔH_{fus} /kJ mol ⁻¹	ΔH_{vap} /kJ mol ⁻¹
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Physical properties reflect intermolecular forces

Table 15-3 shows examples of differences in boiling points.

Why is H₂O > SO₂?

TABLE 15.3 Normal melting points, boiling points, and molar enthalpies of vaporization and fusion at these temperatures and one atm (1.01325 bar) pressure

Compound	Chemical formula	Melting point/K	Boiling point/K	ΔH_{fus} /kJ mol ⁻¹	ΔH_{vap} /kJ mol ⁻¹
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13

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Intermolecular forces (IMFs)

All forces in chemistry are due to attraction or repulsion of electrical charges on the interacting particles, according to

Coulomb's law: $\Delta E \approx \frac{\text{charge}_1 \times \text{charge}_2}{\text{separation}} = E_{\text{sep.}} - E_{\text{for apart} = \infty}$

For opposite charges $\Delta E < 0$ and so the particles are attracted.

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Intermolecular forces (IMFs)

All forces in chemistry are due to attraction or repulsion of electrical charges on the interacting particles, according

Coulomb's law: $\Delta E \approx \frac{\text{charge}_1 \times \text{charge}_2}{\text{separation}}$

For like charges $\Delta E > 0$ and so the particles are repelled.

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15

15

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Intermolecular forces (IMFs)

All forces in chemistry are due to attraction or repulsion of electrical charges on the interacting particles, according

Coulomb's law: $\Delta E \approx \frac{\text{charge}_1 \times \text{charge}_2}{\text{separation}}$

The smaller the separation if the charges, the greater the magnitude $|\Delta E|$.

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16

16

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Intermolecular forces (IMFs)

$\text{Na}^+ \text{Cl}^- \rightarrow \text{NaCl}(s)$

We can use Coulomb's law to understand the attraction of pairs of ions in molecules like NaCl, KBr, etc.

Because the ion separations are small, their interaction energy, ΔE , is very large, on the order of 100s of kJ/mol.

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18

18

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Intermolecular forces (IMFs)

But what Coulomb interactions are possible for interaction of neutral particles?

Handwritten notes: Xe vs. Ne || H₂O vs. SO₂ ||

- Na with Na
- He with He,
- CO₂ with CO₂,
- NH₃ with NH₃,
- C₈H₁₈ with C₈H₁₈,
- etc?

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19

19

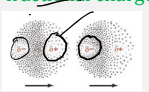
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Intermolecular forces (IMFs)

But what **Coulomb interactions** are possible for interaction of **neutral particles**?

There are three possibilities, in order of **decreasing importance**.

1. Always: **London (van der Waals forces, dispersion forces)**, due to the interaction between **temporary fractional charges**.



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Instantaneous dipoles → London forces

When one atom encounters another closely, the electrical repulsion between the electron clouds is similar to **mismatched (off-resonance) interaction** of light and matter.

The result is the electron clouds of all atoms **always quiver slightly** when they encounter one another.

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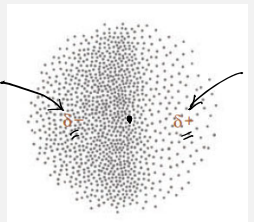
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Instantaneous dipoles → London forces

This quivering means that electron clouds are **momentarily lopsided**, with the result that atom have **momentary electrical dipoles**.



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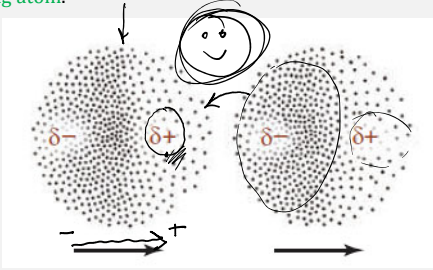
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Instantaneous dipoles → London forces

Should another atom pass nearby, the momentary dipole will **induce a dipole in the neighboring atom**.



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23

23

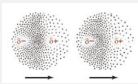
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Intermolecular forces (IMFs)

But what **Coulomb interactions** are possible for interaction of **neutral particles**?

There are three possibilities, in order of **decreasing importance**.

1. Always: **London (van der Waals forces, dispersion forces)**, due to the interaction between **temporary fractional charges**.



All particles interact with one another as a result of London IMF

London IMF are weak because the fractional charges are **small and fleeting**.

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25

25

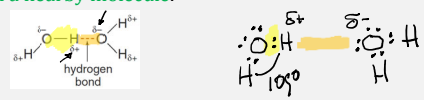
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Intermolecular forces (IMFs)

But what **Coulomb interactions** are possible for interaction of **neutral particles**?

There are three possibilities, in order of **decreasing importance**.

2. Sometimes: **Hydrogen bonding** between **H covalently bonded to N, O, or F** interacting with an **N, O, or F on a nearby molecule**.



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26

26

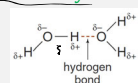
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Intermolecular forces (IMFs)

But what **Coulomb interactions** are possible for interaction of **neutral particles**?

There are three possibilities, in order of **decreasing importance**.

2. Sometimes: **Hydrogen bonding** between **H covalently bonded to N, O, or F** interacting with an **N, O, or F on a nearby molecule**.



$\text{NH}_3 \leftrightarrow \text{NH}_3$, $\text{HF} \leftrightarrow \text{HF}$, $\text{CH}_3\text{OH} \leftrightarrow \text{CH}_3\text{OH}$, etc.

Hydrogen bonds are **weaker and longer** than covalent bonds and ion-ion interactions.

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27

27

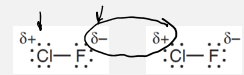
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Intermolecular forces (IMFs)

But what **Coulomb interactions** are possible for interaction of **neutral particles**?

There are three possibilities, in order of **decreasing importance**.

3. Sometimes: **Dipole-dipole interaction** between the **permanent, fractional charges** on nearby **polar molecules**.



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28

28

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Intermolecular forces (IMFs)

But what **Coulomb interactions** are possible for interaction of **neutral particles**?

There are three possibilities, in order of **decreasing importance**.

3. Sometimes: **Dipole-dipole interaction** between the **permanent, fractional charges** on nearby **polar molecules**.

$\delta^+ \text{Cl} \text{---} \text{F} \delta^-$
 $\text{:Cl} \text{---} \text{F:}$

$\delta^+ \text{Cl} \text{---} \text{F} \delta^-$
 $\text{:Cl} \text{---} \text{F:}$

$\text{CH}_3\text{OH} \leftrightarrow \text{CH}_3\text{OH}$, $\text{CH}_3\text{Cl} \leftrightarrow \text{CH}_3\text{Cl}$, $\text{CH}_2\text{Br}_2 \leftrightarrow \text{CH}_2\text{Br}_2$, etc.

Because of the **fractional charges**, dipole-dipole interaction is much **weaker** than **hydrogen bonds** and **than ion-ion interactions**.

$\text{Na}^+ \text{Cl}^-$

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29

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Putting it all together: Relative boiling points

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38

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Relative boiling points

Boiling means particles overcome attraction to their neighbors and depart the liquid.

Relative boiling points reflect **relative importance of intermolecular forces** ...

- London (dispersion)
- Hydrogen bonding
- Dipole-dipole interaction

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39

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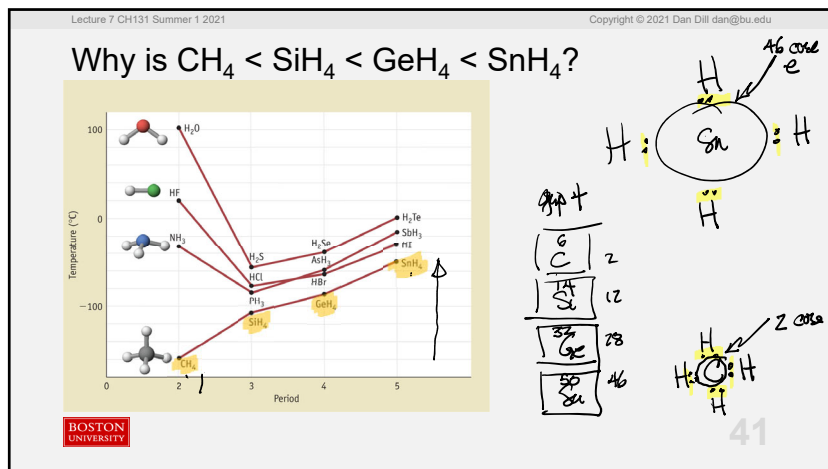
Why is $\text{SnH}_4 < \text{SbH}_3 < \text{TeH}_2$?

Temperature (°C)

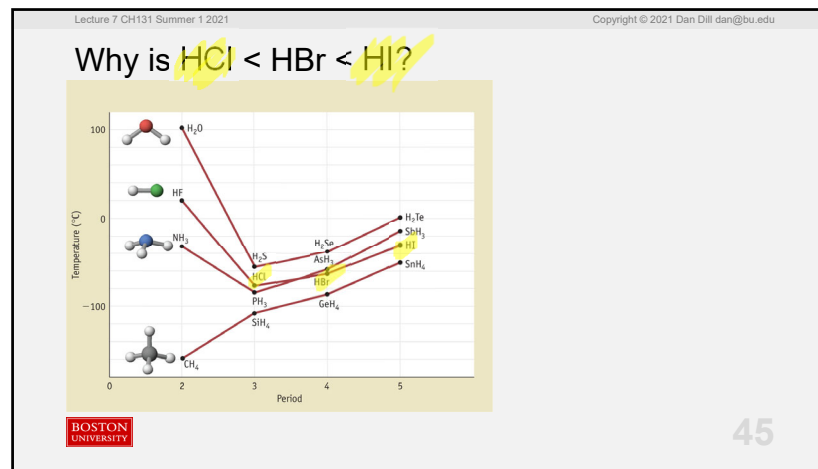
Period

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40



41



45

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[TP] Recall that the greater the electronegativity difference, the greater the polarity. The correct order of polarity of HBr, HCl and HI is (least to most) ...

- 0% 1. $\text{HBr} < \text{HCl} < \text{HI}$
- 0% 2. $\text{HBr} < \text{HI} < \text{HCl}$
- 0% 3. $\text{HCl} < \text{HBr} < \text{HI}$
- 0% 4. $\text{HCl} < \text{HI} < \text{HBr}$
- 0% 5. $\text{HI} < \text{HCl} < \text{HBr}$
- 100% 6. $\text{HI} < \text{HBr} < \text{HCl}$

Handwritten notes: A box with 'H' and an arrow pointing to a vertical stack of boxes containing 'F', 'Cl', 'Br', 'I' with an upward arrow. Another note says '001595'.

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11 of 15

46

46

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Why is $\text{HCl} < \text{HBr} < \text{HI}$?

The order of boiling points of HCl, HBr, and HI is the opposite order of polarity.

How can this be?

Handwritten notes: HCl more ionic character, greater dipole moment, greater ΔEN . HI least ionic character, least dipole, least ΔEN . Electronegativity values: $\text{H}-\text{Cl}$ (+0.6, -0.6), $\text{H}-\text{I}$ (+0.1, -0.1).

Temperature (°C)

Period

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47

47

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Why is $\text{HCl} < \text{HBr} < \text{HI}$?

The London IMF of a larger molecule is greater than the dipole-dipole IMF of a smaller molecule.

Let's see why.

Handwritten notes:
 HI bigger cloud → larger London
 HCl more polar → larger dipole-dipole

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48

48

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London IMF

Sketch the induced dipole in the nearby molecule in each case:

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49

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Dipole-dipole IMF

Sketch a second molecule of the same kind arranged so that it ...

attracts maximally *permanent*

repels maximally

neither attracts nor repels

Handwritten notes for diagram 1: $\sim 33\%$, $\sim 70\%$

Handwritten notes for diagram 2: 33% , $< 10\%$

Handwritten notes for diagram 3: 33% , 15% for T_b

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51

51

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Why is $\text{HCl} < \text{HBr} < \text{HI}$?

The result is that the only time dipole-dipole IMF can be used to predict relative boiling point is if the molecules have comparable size, and so comparable London IMF.

Only then will the residual slight attraction of permanent dipoles be important.

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53

53

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[TP] What is the order or boiling point (lowest to highest) of Br_2 , Cl_2 , I_2 , and ICl ?

0% 1. $\text{Cl}_2 < \text{Br}_2 < \text{I}_2 < \text{ICl}$

→ 100% 2. $\text{Cl}_2 < \text{Br}_2 < \text{ICl} < \text{I}_2$

0% 3. $\text{Cl}_2 < \text{ICl} < \text{Br}_2 < \text{I}_2$

0% 4. $\text{ICl} < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$

0% 5. Not sure

Cl $:\text{Cl}:\text{Cl}:$ smallest

Br $:\text{Br}:\text{Br}:$ = $:\text{I}:\text{Cl}:$

I $:\text{I}:\text{I}:$ largest

001599

11 of 15

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54

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London IMF comparable? Use dipole-dipole IMF

What is the order or boiling point (lowest to highest) of Br_2 , Cl_2 , I_2 , and ICl ?

$\text{Cl}_2 = -34^\circ\text{C}$: smallest electron cloud

$\text{Br}_2 = +58^\circ\text{C}$

$\text{ICl} = +98^\circ\text{C}$: similar-sized electron cloud as Br_2 but polar

$\text{I}_2 = +184^\circ\text{C}$: largest electron cloud

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Why is $\text{NH}_3 > \text{PH}_3 < \text{AsH}_3 < \text{SbH}_3$?

Temperature ($^\circ\text{C}$)

Period

SnH_4
 GeH_4
 SiH_4
 CH_4

SbH_3
 AsH_3
 PH_3

NH_3

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56

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Hydrogen bonding //

Br_2 ICl

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57

57