Gases, Liquids and Solids

Solids are incompressible and rigid and maintain their own shape and volume.
Molecules in a solid are
- are touching
- very ordered
- vibrate within a position but are stationary

Liquids are nearly incompressible and fluid and have their own volume, but conform to the shape of the container.
Molecules in a liquid are
- touching one another
- random
- constantly moving over one another

Gases are highly compressible and fluid and conform to the shape and volume of a container.
Molecules in a gases are
- far apart from one another (much distance between molecules)
- random
- constantly moving in straight line random motion

Changes of state

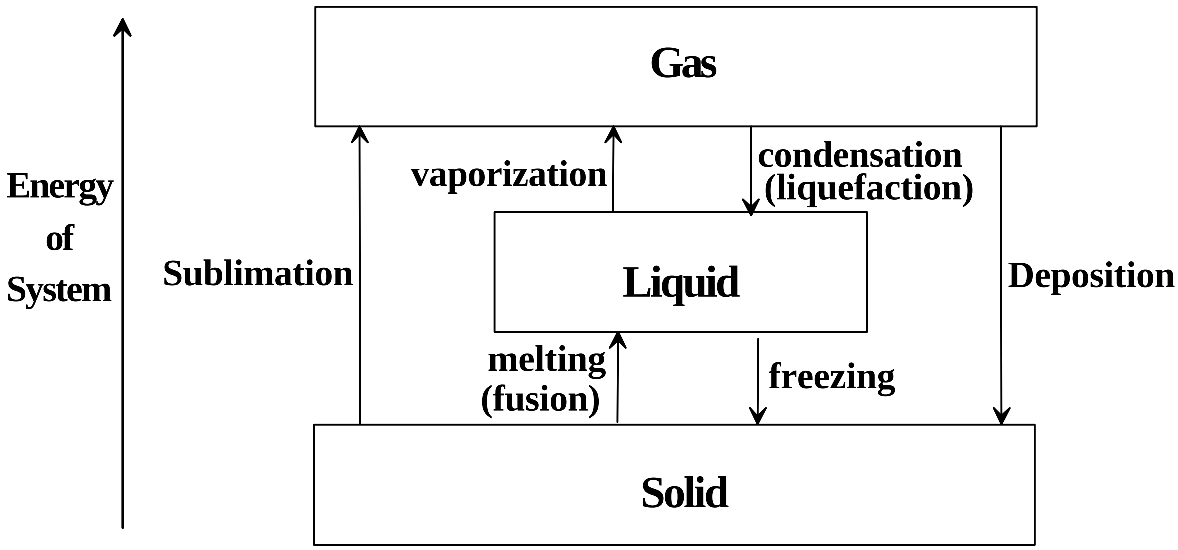
A change of state or phase transition is a change of a substance from one state to another state.

Defining the various phase changes

Phase change	Name of phase change
Solid $\rightarrow$ Liquid	Melting or Fusion
Solid $\rightarrow$ Gas	Sublimation
Liquid $\rightarrow$ Solid	Freezing
Liquid $\rightarrow$ Gas	Vaporization
Gas $\rightarrow$ Liquid	Condensation
Gas $\rightarrow$ Solid	Deposition

The following figure shows the various phase changes between the various states.

Changes of State (phase changes)



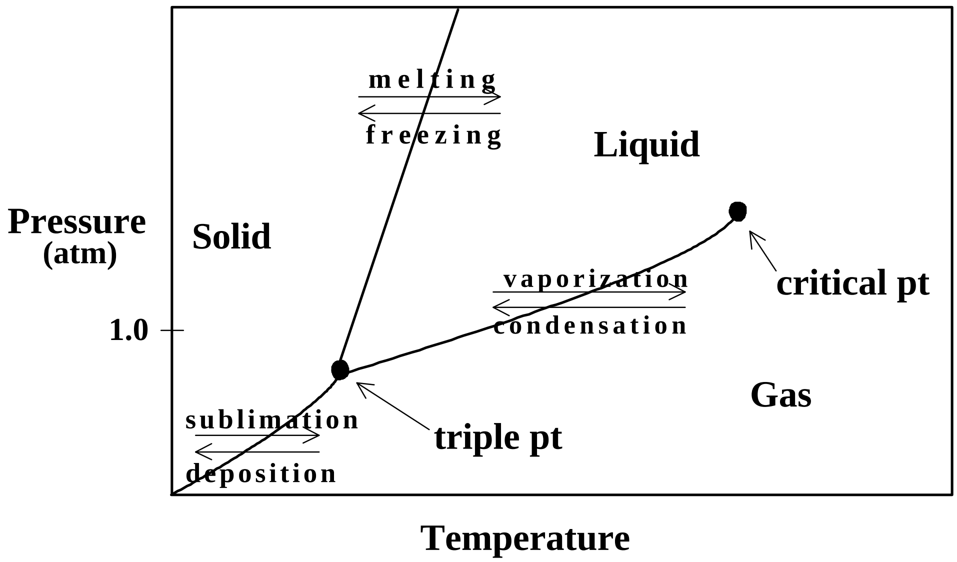
A state that changes towards:

Less order	More order
requires energy	releases energy
overcomes intermolecular forces	gives into intermolecular forces
endothermic	exothermic

Phase Diagrams

Phase diagrams summarize "the conditions at which a substance exists as a solid, liquid or gas"

General Shape



The phase diagram provides information about the physical state of a substance over a wide range of pressures and temperatures and contains the following features.

Regions of the diagram: corresponds to one of the substance's phases (solid, liquid or gas)

Lines between the different phases:
The line separating the solid and liquid phases is the melting point of the substance at different pressures and temperatures
The line separating the liquid and gas phases is the boiling point of the substance at various pressures and temperatures
The line separating the solid and gas phases is the sublimation point of the substance at various pressures and temperatures

Triple point: the pressure and temperature at which all three phases are present at equilibrium

Critical point: the point at which the liquid-gas line ends
(beyond this pt, the liquid and gas phases become indistinguishable)

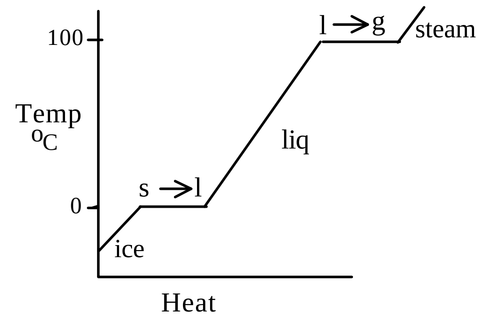
Critical temperature: temp above which the liquid state of a substance no longer exist regardless of pressure

Critical pressure: pressure required to bring about liquefaction at the critical temperature

Normal boiling point (bp) and Normal melting point (mp): bp and mp at 1 atm pressure

Energy in the form of heat (enthalpy)

A change of state involves the removal or addition of energy as heat. During a phase change the heat energy of the substance increases or decreases but the temperature of the substance remains unchanged until the phase change is completed. For example, ice will melt at 0 ºC to the liquid state at 1 atm pressure. The water will not change temperature until all the ice has melted. (see side figure)



Melting

- referred to as fusion
- heat of fusion, ΔH_{fus}: heat required to melt a solid at its mp

e.g. for water

H_2O (s) → H_2O (l) ΔH_{fus} = 6.01 kJ/mol at 0ºC

Vaporization

- heat of vaporization, ΔH_{vap}: heat needed to vaporize a liquid at its bp

e.g. for water

H_2O (l) → H_2O (g) ΔH_{vap} = 40.7 kJ/mol at 100ºC

Note: Why is $\Delta H_{vap} > \Delta H_{fus}$?

The solid → liquid phase change only requires enough energy for molecules to escape sites in the solid (to move past one another). In a solid or liquid the molecules are still touching one another.

The liquid → gas phase change requires enough energy to overcome intermolecular forces (to separate molecules from one another). Molecules in a liquid are still touching one another, while molecules in a gas are separated by great distances.

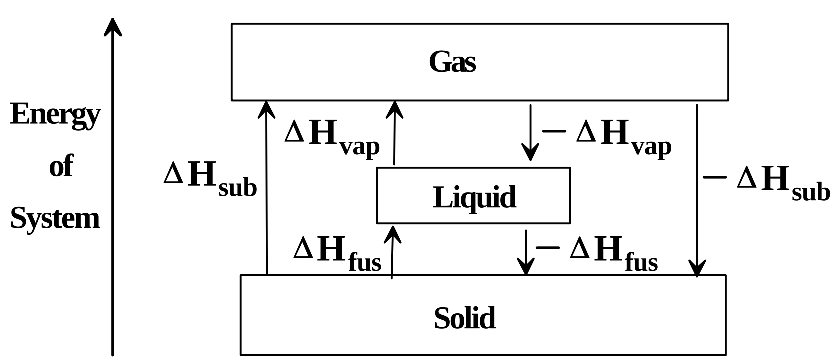
What is the enthalpy of sublimation?

Recall: Enthalpy is a State Function

$$\Delta H_{sub} = \Delta H_{vap} + \Delta H_{fus}$$

Solid → Liquid	ΔH^o_{fus}
Liquid → gas	ΔH^o_{vap}
Solid → gas	ΔH^o_{sub}

Changes of State
and their enthalpy changes:



Examples

Calculate the amount of heat (in kJ) required to convert 74.6 g of water to steam at 100 ^oC. ΔH_{vap} = 40.7 kJ/mol

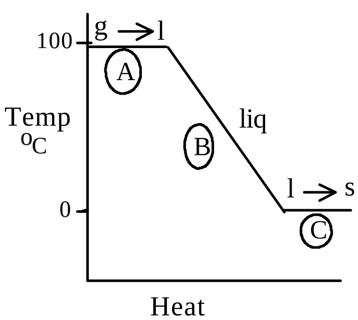
Calculate the amount of heat evolved when 27.2 g of steam condenses at 100 ^oC, cools to 0 ^oC and freezes.

Examples

Calculate the amount of heat (in kJ) required to convert 74.6 g of water to steam at 100 ^oC. ΔH_{vap} = 40.7 kJ/mol

$$74.6\ g\ H_2O\left(\frac{1\ mol\ H_2O}{18.0\ g\ H_2O}\right)\left(\frac{40.7\ kJ}{1\ mol\ H_2O}\right) = 169\ kJ$$

Calculate the amount of heat evolved when 27.2 g of steam condenses at 100 ^oC, cools to 0 ^oC and freezes.



A) $heat = mol(\Delta H_{vap}) = (27.2\,g\,H_2O)\left(\frac{1\ mol}{18.0g}\right)\left(-40.7\frac{kJ}{mol}\right) = -61.5\,kJ$

B) $heat = m(s)(\Delta T) = (27.2\,g\,H_2O)\left(4.18\frac{J}{g\bullet\ ^oC}\right)(0-100\ ^oC)\left(\frac{kJ}{10^3J}\right) = -11.4\,kJ$

C) $heat = mol(\Delta H_{fus}) = (27.2\,g\,H_2O)\left(\frac{1\ mol}{18.0g}\right)\left(-6.01\frac{kJ}{mol}\right) = -9.1\,kJ$

Total heat = heat A + heat B + heat C

– 61.5 kJ + – 11 4 kJ + – 9.1 kJ = – 82.0 kJ

Intermolecular Forces between Molecules

Intermolecular Forces (IMF) have an effect on various properties (mp, bp, etc.) of molecules.

1) Covalent Molecules
   a) Intramolecular force (force within a molecule)
      Within a molecules, the **covalent bond** is the force holding atoms together.
      covalent bond is the sharing of a pair of e-

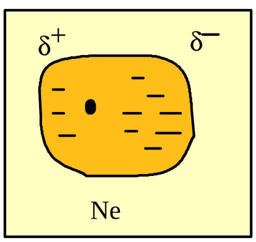
   b) Intermolecular forces (forces between covalent molecules)

      3 Types
      A) London Dispersion Forces (LDF) or London Forces
      B) Dipole/Dipole
      C) Hydrogen Bonding (H-bonding)

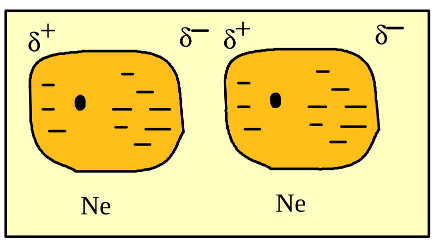
      Describing the 3 different intermolecular forces between covalent molecules

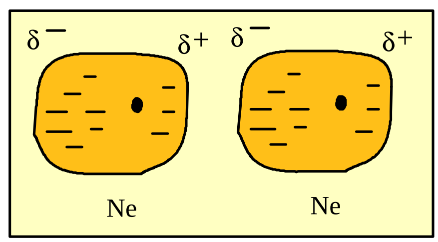
A) London Dispersion Forces (LDF)

- exist between atoms and molecules
- motion of e in an atom or molecules creates an *instantaneous dipole moment*
- very weak



A single neon atom has a region of electron density that is momentarily greater than another. This atom is exhibiting an instantaneous dipole.





When two neon atom are close to one another the momentarily greater electron density region of one atom will induce an instantaneous dipole in the adjacent atom.

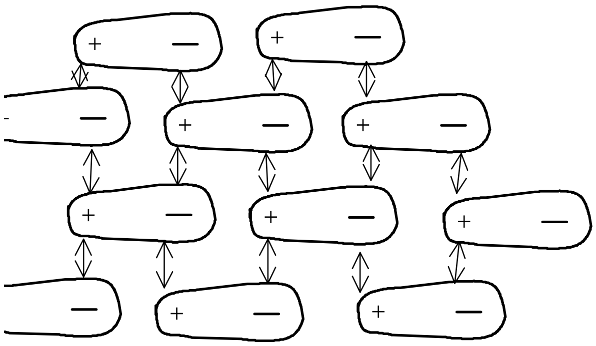
The strength of the London Dispersion Forces is influenced by the

1) molar mass of the particles
   The strength of LDF increases with an molar mass
   Particles with a greater mass has more atoms thus more electrons

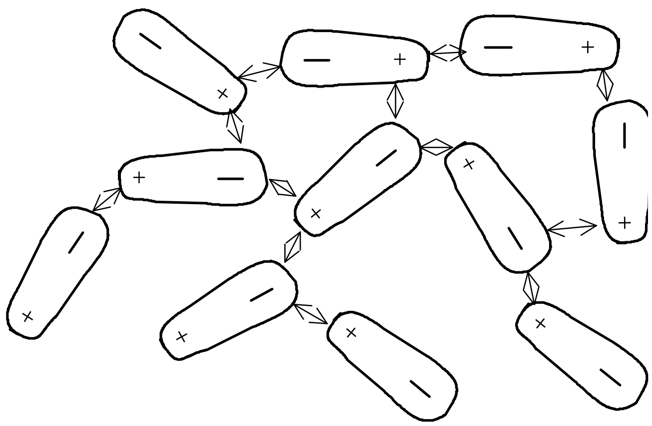
2) molecular shape of molecules with the same molar mass
   The strength of LDF increases with the less compactness of molecules
   Shapes that allow more points of contact have more area over which electron clouds can be distorted.

B) Dipole/Dipole

- exist between polar molecules
- partial positive pole of one molecules attracts a partial negative pole of another molecule



In a solid, the molecules are lined up where the negative end of one molecule faces the positive end of another molecule



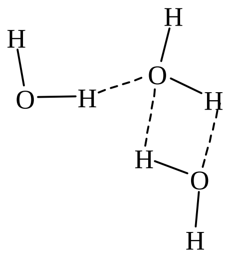
In a liquid the molecules are random. The negative end of a dipolar molecules is found near a postive end of another dipolar molecule

Strength of dipole/dipole interactions

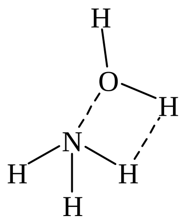
for molecules with approximately the same size and molar mass depends on the polarity of the molecules. The strength of dipole/dipole interaction increases with polarity

C) Hydrogen Bonding (H-bonding)

- special dipole/dipole force
- occurs between a H atom which is attached to N, O, or F and an atom of N, O, or F on another molecules



H-bonding occuring between water molecules. H-bonding is represented by the dotted lines.



H-bonding can also occur between a molecules of ammonia and water.

Comparing the relative strengths of the IMF found between covalent molecules

of the three IMF just discussed the strongest is H-bonding, the second strongest is dipole/dipole, and the weakest of the three is London dispersion forces.

H-bonding > dipole/dipole > London Forces

The next three IMF exist between structural units (atoms or molecules) in the solid state

2) Ionic compounds

An ionic compound consists of cations and anions

The attraction between ions in one formula unit to another formula unit in an ionic solid is the **Ionic Bond**

Relative strength of ionic bond

2 criteria

1) size of ions

The strength of the ionic bond increases with a decrease in the size of the ions

2) Magnitude of charge

The ionic bond strength increases with magnitude of charge

To find the magnitude of charge multiply together the charges on each ion in the formula unit

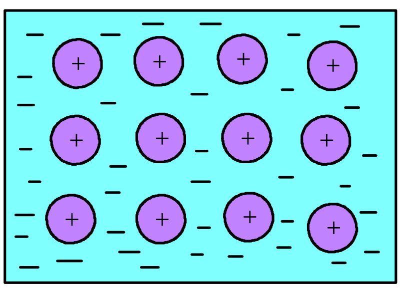
e.g. $NaCl \rightarrow Na^{+} + Cl^{-}$ $(+1) \times (-1) = -1$

$MgO \rightarrow Mg^{2+} + O^{2-}$ $(+2) \times (-2) = -4$

Since MgO has the large magnitude of charge, the ionic bond between MgO formula units are stronger than the ionic bond between NaCl formula units

3) Metallic solids

A solid that consists of positive cores of atoms held together by a surrounding "sea" of delocalized valence electrons (metallic bonding)

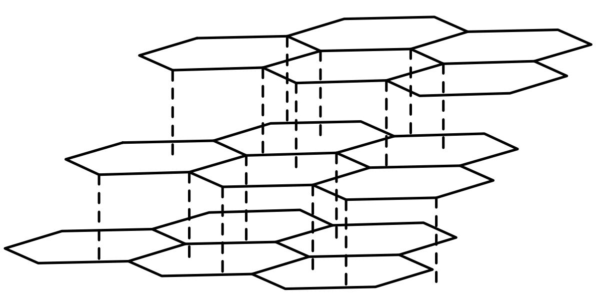


Each circled positive charge represents the nucleus and inner electrons of a metal atom. The negative charges surrounding the positive metal ions indicates the mobile sea of electrons

4) Network Covalent Solids or Macromolecules

A solid that consists of atoms held together in large networks or chains by covalent bonds.

Seven common macromolecules are $C_{graphite}$, $C_{diamond}$, Si, Ge, SiO_2, SiC, BN



In graphite, the carbon atoms are covalently bound in sheets of linked hexagons. Delocalized π electrons give high electrical conductivity in the planes of the sheets, and weak dispersion forces between the sheets make graphite soft.

Comparison of types of compounds, various forces and properties

Type of compound	Intermolecular Forces	mp	bp	Conductivity
Covalent (molecular)	London dispersion Dipole/Dipole H-bonding	very low	low to medium	insulators
Metals	Metallic bonds	low to medium	medium to high	conductors
Ionic	Ionic bond	high	high to very high	conductors in molten state
macromolecules (covalent network solids) $C_{graphite}$, $C_{diamond}$, Si, Ge, SiO_2, SiC, BN	Covalent bond	Extreme (decomposes)		only graphite conducts

The above table list the intermolecular forces from weakest to strongest. The melting point (mp), boiling point (bp) and conductivity vary between the various types of compounds due to the different intermolecular forces (IMF).

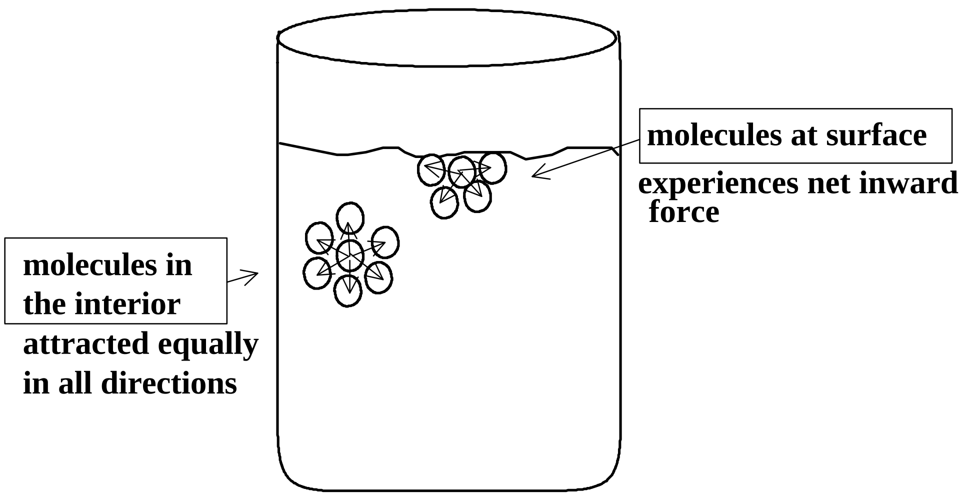
The covalent molecules can have one to all three IMF occurring. The strongest of these will be the dominating IMF for that covalent molecule. mps and bps are lowest for molecules only exhibiting LDF and highest for the covalent molecules with H-bonding as the dominating IMF.

Covalent molecules	Dominating IMF
nonpolar molecules	London dispersion forces
polar molecules	dipole/dipole
polar molecules with a H atom attached to N, O, or F	Hydrogen bonding

Effect of Intermolecular Forces (IMF) on Properties of Substances

Liquid State

1) Surface Tension (of a liquid)
   - amount of energy required to stretch or increase the surface of a liquid by a unit area



- inward force makes molecules at the surface pack closely together
- liquid at the surface behave as a "skin" of water
- surface tension of a substance increases (↑) as IMF ↑
- The stronger the forces between the particles in a liquid, the greater is the surface tension

2) **Viscosity**
   - measure of a fluid's resistance to flow
     the larger the viscosity is the thicker the liquid
   - viscosity ↑ as IMF ↑
   - viscosity ↓ as Temp ↑
     At higher temperature molecules move faster and can overcome intermolecular forces more easily, therefore the restance to flow decreases

Solid State

3) **Hardness**

- force needed to deform a solid
- depends on how easily the structural units of a solid move relative to one another
- the stronger the interactive forces are between structural units, the harder the solid

hardness ↑ as IMF ↑

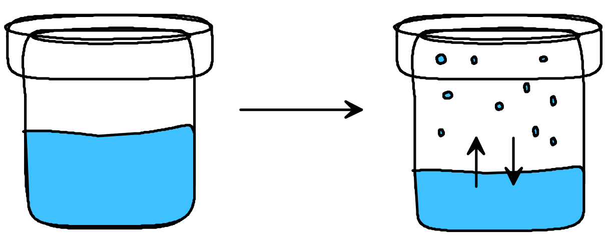
type of compound	Hardness	
Covalent	soft	brittle
Metals	soft to hard	malleable
ionic	hard	brittle
macromolecules	very hard	

Liquids & some Solids

4) **Vapor Pressure**

- the partial pressure of a vapor over the liquid (or solid), measured at equilibrium

Experiment:
- container of liquid (with cap)
- evacuated of air
- liquid evaporates
- evaporation seems to cease when equilibrium has been reached:
  amount of liquid molecules → gas phase
  is the same as gas molecules → liquid phase
- pressure exerted by the vapor over the liquid is vapor pressure



- Vapor pressure ↑ as Temp ↑
  as the temperature increases, more molecules have enough energy to escape the liquid phase and less molecules are moving slow enough to be recaptured by the liquid phase.
- Vapor pressure ↓ as IMF ↑
  molecules with weaker intermolecular forces vaporize more easily,
  therefore have higher vapor pressures

5) Critical Temperature and Critical Pressure

Critical Temperature
- highest temp at which a substance can exist as a liquid

Critical Pressure
- pressure required to bring about liquefaction at this critical temp
- vapor pressure at the critical temp

Both critical temp & critical pressure ↑ as IMF ↑

6) Melting pt (mp) and Boiling pt (bp)

mp: temp at which a solid changes to a liquid
normal mp: mp at 1 atm pressure

bp: temp at which vapor pressure of the liquid equal the external pressure on the surface of the liquid
normal bp: bp at 1 atm pressure (external)

Both mp and bp ↑ as IMF ↑

7) ΔH_{vap} & ΔH_{fus}

ΔH_{vap}: the energy required to vaporize a liquid at its bp

ΔH_{fus}: the energy required to melt a solid at its mp

Both ΔH_{vap} & ΔH_{fus} ↑ as IMF ↑

Summary of the effects of intermolecular forces on various properties of substances

Property		IMF
surface tension	↑	↑
viscosity	↑	↑
hardness	↑	↑
critical temp & critical pressure	↑	↑
mp & bp	↑	↑
ΔH_{vap} & ΔH_{fus}	↑	↑
vapor pressure	↓	↑