

4.1, 4.2

water

Plays dominant role in radiation

All three phases emit and absorb in longwave radiation

Some shortwave (solar) radiation is absorbed by all phases of water

Principal role in the shortwave radiation balance

Through the scattering of solar radiation by clouds and reflection by surface ice and snow

Large heat capacity of the ocean allows it to transport large amounts of heat

Water is an important modulator of the Earth's climate

Liquid phase → Highest specific heat

Molecular viscosity → Less than most liquids

Highest value of the latent heat {
of evaporation
Of fusion

Important for transfer of heat and
water within the atmosphere

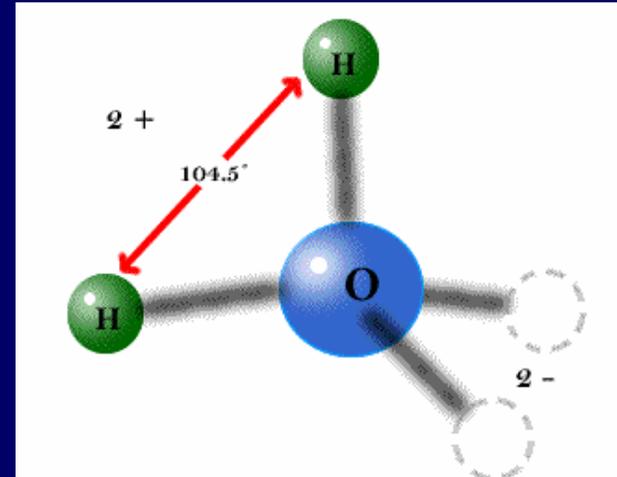
Highest surface tension → Controlling formation and
behavior of cloud drops

Dissolves more substances and in greater quantities

2 hydrogen atoms on one side of a water molecule

the oxygen, being a stronger electron grabber than hydrogen

is able to pull the electrons shared with each hydrogen towards it.



The result is an unequal sharing of the electrons

This makes a water molecule polar

the oxygen end of the molecule has more electrons (negative charge)

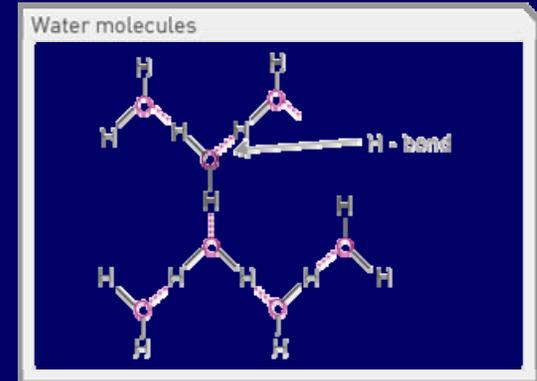
the hydrogen end has a slightly more positive end

electromagnet

The negative end is able to attract positive ions or the positive end of other polar molecules.

The positive end is able to attract negative ions or the negative end of other polar molecules

water is able to dissolve many substances, and it is thus called a universal solvent.



This permanent dipole moment gives rise to many electromagnetic absorption lines

Very important molecule in atmospheric radiative transfer

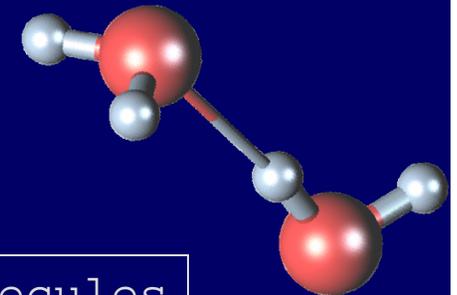
Also influences the heat capacity

Water vapor at high concentrations or near condensation does not behave like an ideal gas

Definition of ideal gas

The gas molecules occupy no volume.

There are no interactive forces between the molecules



If the gas molecules occupy a volume because of their finite size, this volume will be approximately independent of pressure

Excluded volume

The van der Waals equation of state

$$\left(p + \frac{an^2}{V}\right)(V - nb) = nR^*T$$

Semi-empirical relation that accounts for the effects of the excluded volume and the intermolecular forces

The ideal gas approximation for water vapor under atmospheric conditions result in an error of less than 1%

The van der Waals equation of state provides a much better representation of the state of water vapor as it approaches condensation

Thermodynamic degrees of freedom

Homogeneous system



Uniform chemical composition whose intensive properties are uniform throughout



Only one phase

Heterogeneous system



Made up of two or more homogeneous parts with abrupt changes in properties at the boundaries of these parts

Distinct phase



Each physically or chemically different, homogeneous and mechanically separable part of a system

Liquid water and ice

Mix of gases

Water and oil

Water and alcohol

Sugar dissolved in water

Two-phase

one-phase

Two-phase

one-phase

one-phase

Components

The minimum number of distinct chemical species necessary to specify completely the chemical composition of all the phases in the system

Some thermodynamic systems

example	components	phases
Liquid water with ice	1	2
Mixture of two gases	2	1
Oil and vinegar	2	2
Water and alcohol	2	1
Sugar in water	2	1
Sand in water	2	2
Two blocks of copper	1	1

Number of components

χ

Number of phases

φ

systems

● Moist air (dry air + water vapor):

$$\chi = 2; \varphi = 1$$

● Liquid cloud (dry air + water vapor + liquid water drops):

$$\chi = 2; \varphi = 2$$

● Cloud drops (liquid water + a soluble aerosol particle)

$$\chi = 2; \varphi = 1$$

● Mixed-phase cloud (dry air + water vapor + liquid water drops + ice particles)

$$\chi = 2; \varphi = 3$$

● Ice cloud (dry air + water vapor + ice particles)

$$\chi = 2; \varphi = 2$$

● Ocean (water + salt, with or without sea ice)

$$\chi = 2; \varphi = 1, 2$$

Thermodynamic degrees of freedom of the system

f

The number of the intensive state variables that can be independently varied without changing the number of phases.

→ Total number of intensive variables which can define each phase

$$\chi - 1 + p + T$$

→ Total number of intensive variables defining the system

$$\varphi(\chi - 1) + p + T$$

→ Number of variables that cannot be independently varied

$$\chi(\varphi - 1)$$

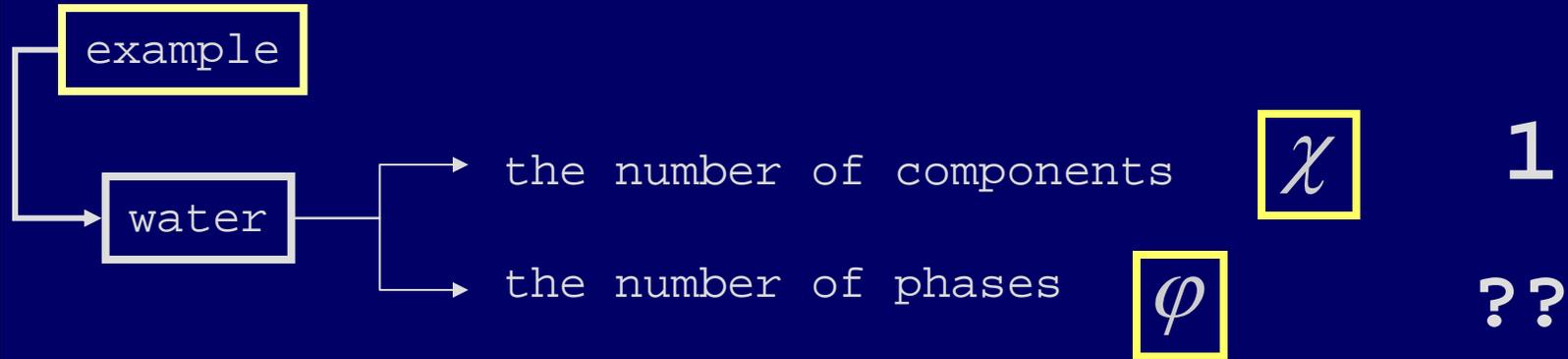
Gibbs phase rule

- Relate the number of degrees of freedom f
- the number of phases φ
- and the number of components χ

$$f = 2 + \varphi(\chi - 1) - \chi(\varphi - 1) = \chi - \varphi + 2$$

Refers to the degrees of freedom associated with temperature and pressure of all phases

Determine the number of intensive variables which may be freely specified in determine the state, without changing the number of components or phases



$$f = \chi - \varphi + 2$$

$$f = 1 - \varphi + 2$$

$$f = 3 - \varphi$$

Three possibilities

$$\varphi = 1, f = 2$$

Bivariant system

2 variables completely specify the state (e.g., water vapor)

$$\varphi = 2, f = 1$$

Univariant system

Liquid and vapor in equilibrium

$$\varphi = 3, f = 0$$

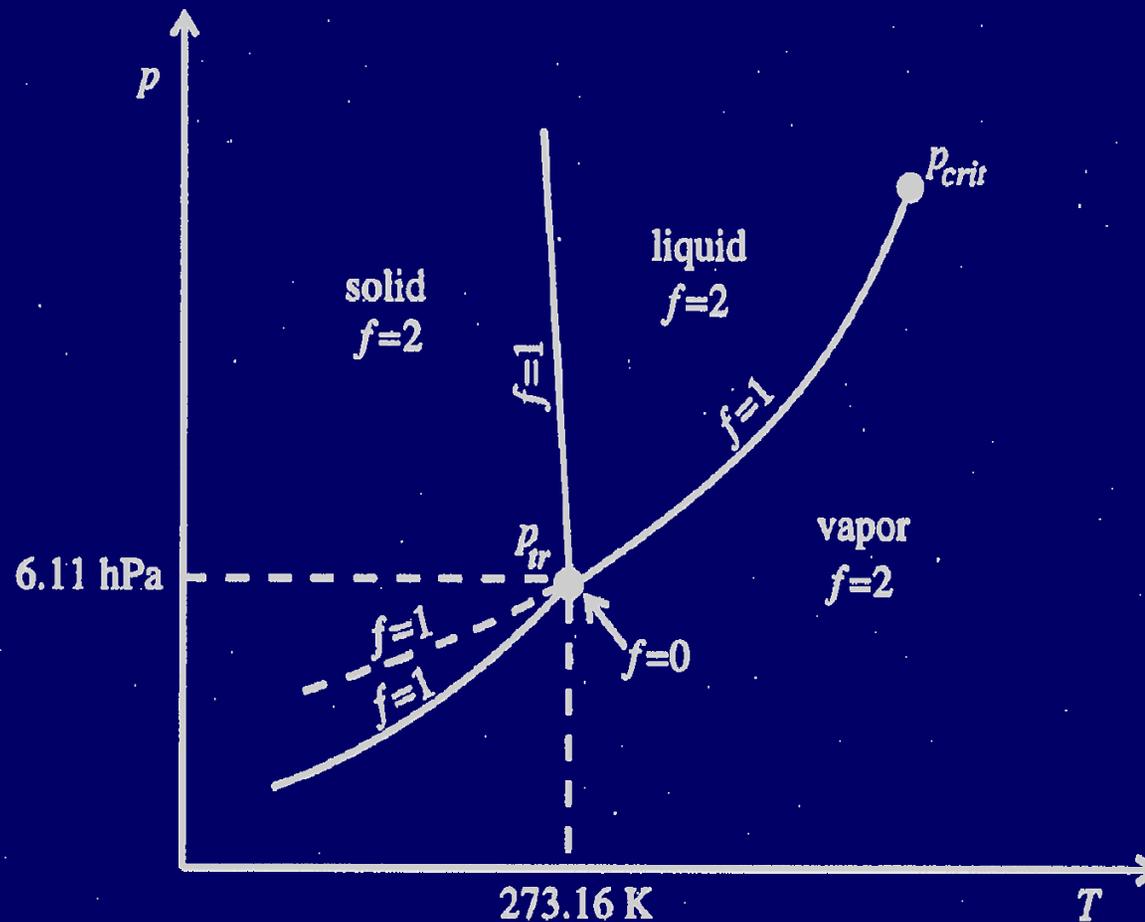
Invariant system

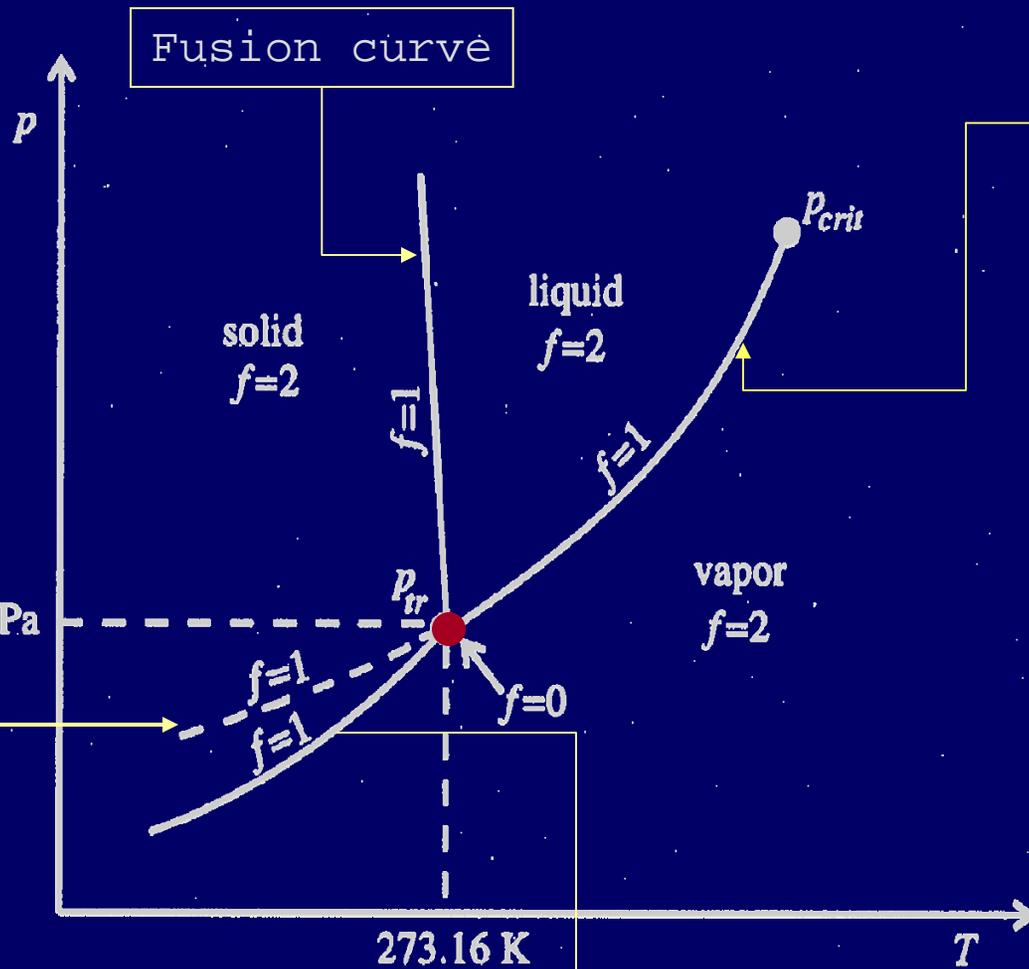
Only occurs at the triple point

Maximum number of degrees of freedom of one component system is 2

Any one-component system can be represented by a two-dimensional diagram

p, T Diagram for water





Fusion curve

Vapor pressure curve of liquid water

$$P_{crit} = 218.8\text{ atm}$$

$$T_{crit} = 647\text{ K}$$

liquid phase is no longer distinguishable from the vapor phase

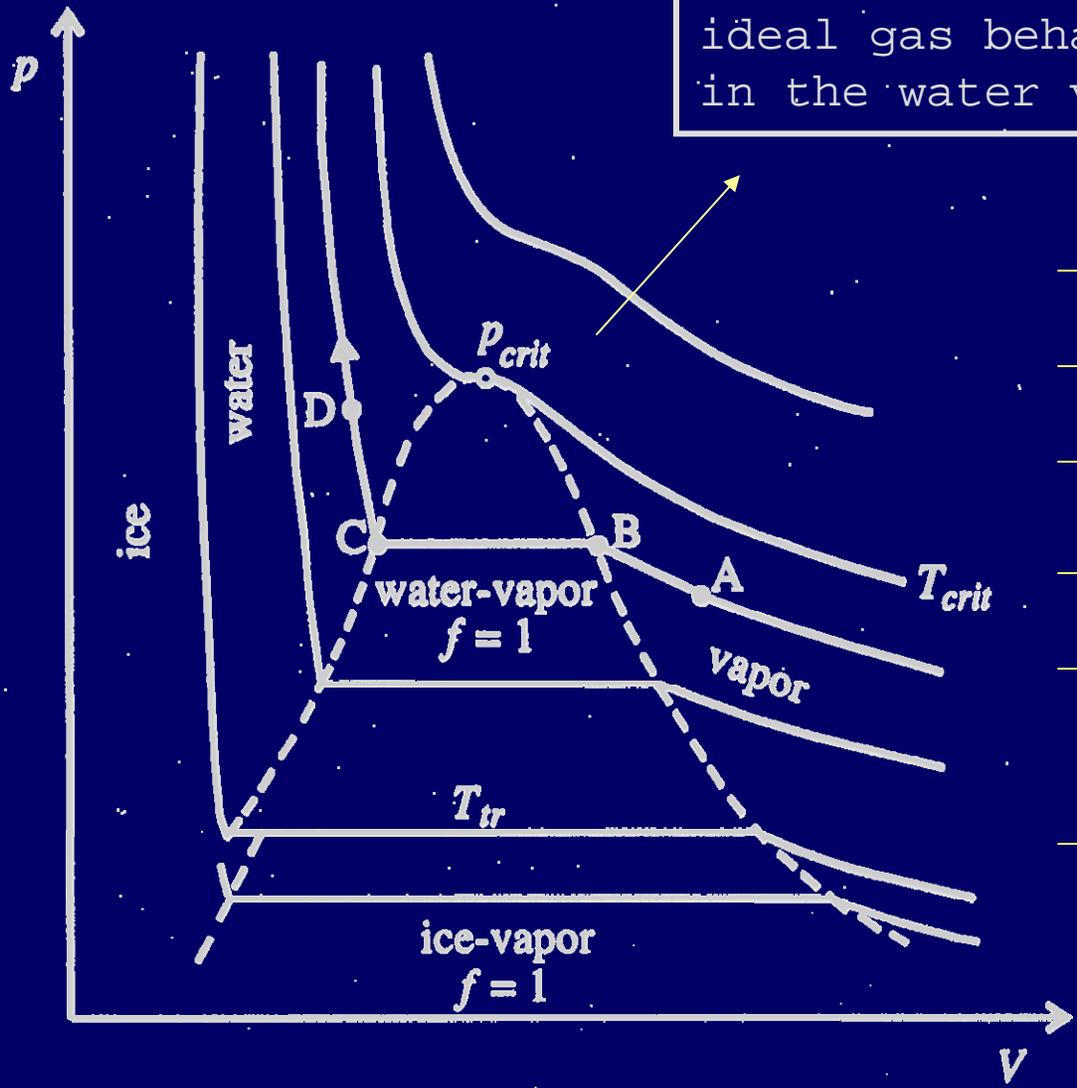
Liquid water can be cooled below its freezing point without solidifying (supercooled water)

Sublimation-pressure curve of ice

p, V Diagram for water

Lines isotherms

Corresponds to ideal gas behavior in the water vapor



- Vapor at point A
- Isothermally compressed
- At B condensation begins
- Liquid forms
- Volume decrease and latent heat is release
- Point C when all vapor has condensed into liquid