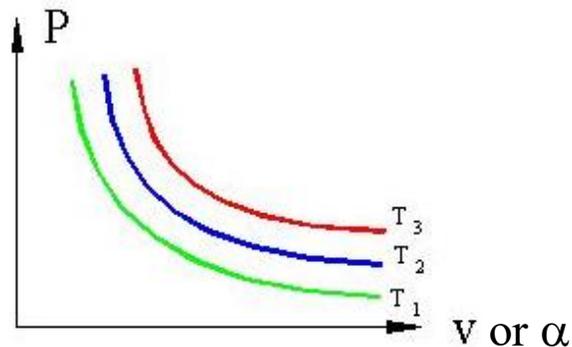# Lecture 14 The Water-Air System

(4.1 and 4.2 of Hess – The Water-Air System)
(4.1: Isotherms on the Phase Diagram; 4.2: Thermal Properties of Water Substance)

[For equation editor, cut and paste: $dq = 0$]

14.1 Isotherms on the Phase Diagram

For an ideal gas, isotherms on a α-p diagram are hyperbolas, i.e.
$p\alpha=RT$=constant.

For water vapor sufficiently far from condensation or sublimation, its behavior is nearly as that of an ideal gas.
Thus, its isotherms on an α-p diagram are also close to hyperbolas.

However, unlike other permanent gases, water may exist in different phases, such as gaseous (water vapor), liquid (water), and solid phase (ice) on our planets.

The phase diagram or α-p diagram of water may be sketched as the following (adopted from Fig. 4.1, p. 40 of Hess).
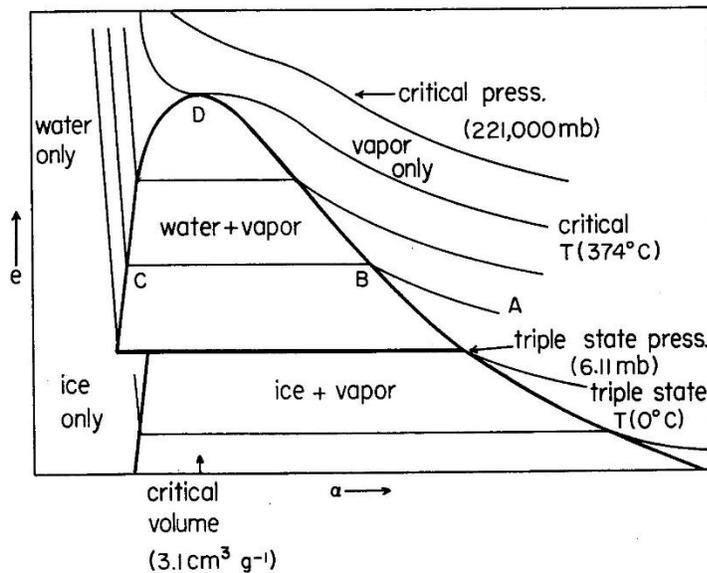
critical press.
(221,000 mb)

water
only

D

vapor
only

water + vapor

critical
T(374°C)

e

C

B

A

triple state press.
(6.11 mb)
triple state
T(0°C)

ice
only

ice + vapor

critical
volume
(3.1 cm³ g⁻¹)

α⟶

FIG. 4.1. Phase diagram of water substance with specific volume, α, and pressure, e, of water substance as coordinates. The heavy lines separate the various phases.

Major characteristics of the above figure may be briefly described as follows.

(1) About the axes:

α = specific volume,

e = pressure of water substance

(in all three phases and possible mixtures of ice, liquid and/or vapor, not just gaseous state).

(2) There are three different types of curves:

- Hyperbolic curves (upper right portion of the figure)
- Near horizontal lines (central portion of the figure)
- Near vertical lines.

(3) We know that

- A straight line parallel to horizontal (α) axis represents an isobaric process
- A straight line parallel to the vertical (p or e) axis represents an isosteric process
- An isothermal process is represented by a hyperbola.

Thus these three types of curves represent three different processes of the water substance.

(4) Processes of A ⟹ B ⟹ C
Consider a water substance is initially located at A has a temperature far above the triple point (273.16 K) slightly higher than freezing point (273.15 K) and far below the critical point (647 K or 374°C), and is present in the form of vapor (gaseous state, not saturated).

If the pressure increases, the water vapor is compressed when the temperature remains constant. So the specific volume decreases (or the density of water substance increases). During this period, the isotherm is hyperbolic in the figure (similar to an ideal gas).

When it reaches point B, i.e., the density of the water vapor becomes so high that a slight further increase of pressure will cause condensation. The water substance will then evolve from B to C without significant increase in pressure, but a dramatic decrease in specific volume. Thus, from B to C, the isotherm is nearly horizontal and parallel to the α axis. This constant pressure is called the saturation vapor pressure. At this particular pressure, vapor and liquid water can coexist.

When the pressure continues to increase, specific volume (density) of the water decreases (increases) slightly because liquid water is almost incompressible. So, the isotherm is almost vertical and parallel to the p-axis.

(5) Starting from the triple point, where the water vapor, water and ice are able to coexist, a slight increase in pressure will condense the water vapor into both liquid water and ice.

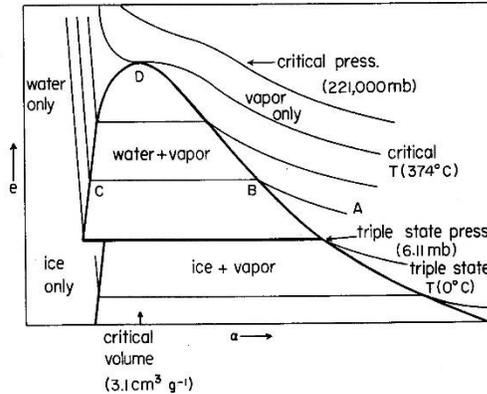The saturation pressure is 6.11mb, and the temperature is 273.16 K at the triple point.

FIG. 4.1. Phase diagram of water substance with specific volume, α, and pressure, e, of water substance as coordinates. The heavy lines separate the various phases.

(6) For the water vapor initially below the triple point and to the right of the boundary separating the "ice+vapor" and "vapor" phases, only solid ice forms when the pressure increases to the point of saturation, and ice, vapor coexist at the saturation pressure.

When the pressure continues to increase, specific volume (density) of the ice decreases (increases) slightly because the ice is almost incompressible. So the isotherm in the solid phase is almost vertical and parallel to the p-axis.

(7) Point D: This is the so called the critical point. The pressure at this point is called critical pressure and the temperature at this point is called critical temperature.

They are called critical since above the critical temperature, no liquid water or ice can exist. Water substance can only exist in the form of vapor. However, to the right of D, vapor exists. To the left of D, liquid water exists. At D, vapor and liquid water can hardly be distinguished because the density

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of the vapor is almost the same as the density of liquid water at such a pressure and temperature. The surface tension of the vapor-water interface becomes zero.   (3/29/16)
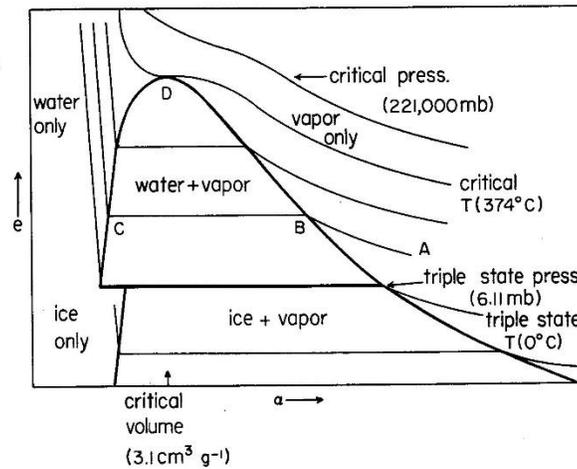

FIG. 4.1. Phase diagram of water substance with specific volume, a, and pressure, e, of water substance as coordinates. The heavy lines separate the various phases.

(8)   Extension of the above concept to other substances.

Compound	T_c (K)	p_c (atm*)	α_c (m³/kg)
Nitrogen	126.2	33.5	0.0110
Oxygen	154.8	50.1	0.0158
Argon	151.0	48.0	6.453×10^{-3}
Carbon Dioxide	304.2	72.9	7.782×10^{-3}

*1 atmosphere=1013.25 mb

Nitrogen, Oxygen, and Argon are permanent gases (i.e. always stay in gas phase) because their critical temperatures are far below the normal temperature in the atmosphere.

CO_2 has a critical temperature within the limit of atmospheric temperature, but there is only a small amount of it in the earth's atmosphere, so within the atmospheric pressure and temperature, its density never become large enough to condense. It does condense in the Venus' atmosphere

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though, due to its abundance there (composed by 95% CO_2, less than 5% N_2 and Ar, and .004% O_2 by volume). Near the cloud top of the Venus atmosphere, $T\sim240K$ and $p\sim100$ mb. Near surface, $T\sim700K$, $p=8.1\times10^3\, mb$.

14.2 Thermal Properties of Water Substance

14.2.1 Specific volume

Specific volume of water and ice vary very slightly with temperature. Thus, they may be considered as constants with respect to T.

α_{ice} at $0°C = 1.091\times10^{-3}\, m^3kg^{-1}$;

α_{water} at $0°C = 1.0002\times10^{-3}\, m^3kg^{-1}$.

Note that at $0°C$, the density of ice is smaller than the density of liquid water. That is, ice is lighter than the liquid water. This property of water substance is kind of counter-intuitive since usually the solid phase has a higher density.

Table 4.1 (Hess)
Departure of Water Vapor from Ideal Conditions

DEPARTURES OF WATER VAPOR FROM IDEAL CONDITIONS

Temperature (°C)	e_s (mb)	α_v, ideal/α_v
−10	2.86	1.0003
0	6.11	1.0005
10	12.27	1.0008
20	23.37	1.0012
30	42.43	1.0018
40	73.78	1.0027

Compound	T_c (K)	p_c (atm*)	α_c (m³/kg)
Nitrogen	126.2	33.5	0.0110
Oxygen	154.8	50.1	0.0158
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*1 atmosphere=1013.25 mb

Nitrogen, Oxygen, and Argon are permanent gases (i.e. always stay in gas phase) because their critical temperatures are far below the the normal temperature in the atmosphere.

Thus, the water vapor is behaves almost like an ideal gas, within 1% of the values for ideal gas.

14.2.2 Specific heat

The specific heat capacity at constant pressure (c_v is difficult to measure for liquid and solid phases) varies slowly with temperature.

T	c_p (J K^{-1} kg^{-1})
0°C	4218
5	4203
17.5	4181
30	4178

Thus, c_p of water may be treated as a constant in practical applications. Note that c_p decreases as T increases since less heat is required to heat to the same amount of temperature when the temperature is higher.

At low vapor pressures, the gas constant, and specific heat capacities for water vapor are:

R_v = 461 J K^{-1} kg^{-1}
c_{vv} = $3R_v$=1383 J K^{-1} kg^{-1}
c_{pv}=$4R_v$=1844 J K^{-1} kg^{-1}

These numbers are not constant with respect to T. However, the air mixes with only a very small amount of vapor (less than 0.04% in mass), the change in c_{vv}, or c_{pv} will not affect the mixture of moist air significantly. Therefore, c_v and c_p of the moist air may be treated as constants in practical applications.

(4/6/17)