3. Single-Component Two-Phase Systems (Vapor Pressure)

You can understand the behavior of single-component two-phase systems by examining the phase diagram of the component of interest. For example, consider the p*-versus-diagram (at constant $\hat{V}$) for water shown in Figure 1 in previous literature. The relationship between temperature and pressure for steam and liquid water phases in equilibrium is represented by the line from the triple point up to point B. In the remainder of this section, we will explain how to determine values for the vapor pressure given the temperature, or the temperature given the vapor pressure.

3.1 Prediction via Equations

You can see from Figure 1 (line AB) that the function of p* versus T is not a linear function (except as an approximation over a very small temperature range). Many functional forms have been proposed to predict p* from T, but we will use the Antoine equation—it has sufficient accuracy for our needs, and coefficients for the equation exist in the literature for over 5000 compounds:

So, **Antoine equation** is equation that relates vapor pressure to absolute temperature.

$$\ln(p^*) = A - \frac{B}{C + T}$$

where A, B, C = constants for each substance
T = temperature, kelvin

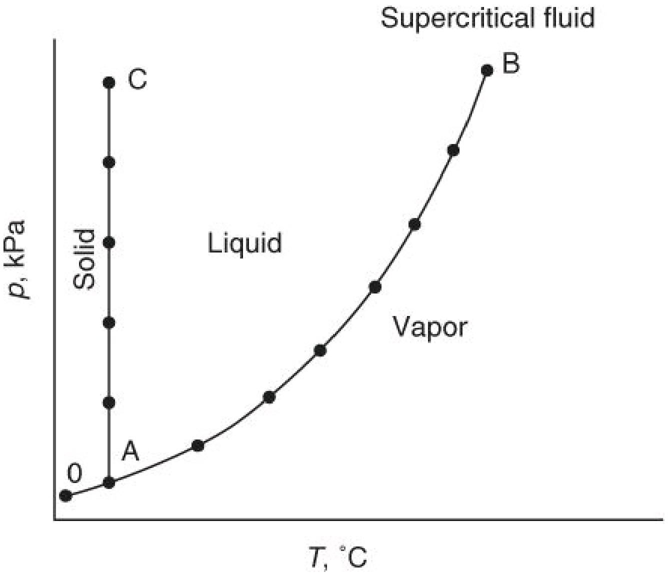


Figure 1. Results of the experiment of heating at constant volume shown on a phase diagram (p versus T at constant $\hat{V}$)

Refer to Appendix G (available online; see Preface, page xvi) for the values of *A, B,* and *C* for various compounds.

Name	Formula	Range (K)	*A*	*B*	*C*
Acetic acid	$C_2H_4O_2$	290–430	16.8080	3405.57	–56.34
Acetone	C_3H_6O	241–350	16.6513	2940.46	–35.93
Ammonia	NH_3	179–261	16.9481	2132.50	–32.98
Benzene	C_6H_6	280–377	15.9008	2788.51	–52.36
Carbon disulfide	CS_2	288–342	15.9844	2690.85	–31.62
Carbon tetrachloride	CCl_4	253–374	15.8742	2808.19	–45.99
Chloroform	$CHCl_3$	260–370	15.9732	2696.79	–46.16
Cyclohexane	C_6H_{12}	280–380	15.7527	2766.63	–50.50
Ethyl acetate	$C_4H_8O_2$	260–385	16.1516	2790.50	–57.15
Ethyl alcohol	C_2H_6O	270–369	18.5242	3578.91	–50.50
Ethyl bromide	C_2H_5Br	226–333	15.9338	2511.68	–41.44
n-Heptane	C_7H_{16}	270–400	15.8737	2911.32	–56.51
n-Hexane	C_6H_{14}	245–370	15.8366	2697.55	–48.78
Methyl alcohol	CH_4O	257–364	18.5875	3626.55	–34.29
n-Pentane	C_5H_{12}	220–330	15.8333	2477.07	–39.94
Sulfur dioxide	SO_2	195–280	16.7680	2302.35	–35.97
Toluene	$C_6H_5CH_3$	280–410	16.0137	3096.52	–53.67
Water	H_2O	284–441	18.3036	3816.44	–46.13

Example 1. Prediction of vapor pressure using Antoine equation

Calculate the vapor pressure of benzene at 50°C using the Antoine Equation. Also estimate the normal boiling point of benzene.

Solution

Antoine Equation $\ln(p^*) = A - \dfrac{B}{C+T}$

From Appendix G in the text the coefficients are

Benzene: $A = 15.9008$ $T = K$

$B = 2788.51$ $p^* = \text{mmHg}$

$C = -52.36$

a. Vapor Pressure of benzene at 50°C

$$\ln(p^*) = 15.9008 - \frac{2788.51}{-52.36 + (50 + 273)}$$

$$p^* = \mathbf{270\ mmHg\ abs}$$

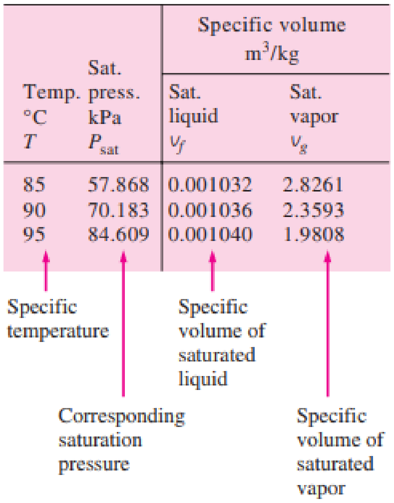
b. At the boiling point the vapor pressure is 1 atm (760 mmHg abs.)

$$\ln(760) = 15.9008 - \frac{2788.51}{-52.36 + T}$$

Solving, T = **353.3K**

3.2 Retrieving Vapor Pressures from the Tables

The vapor pressures of substances listed in tables in handbooks, physical property books, and websites. We use water as an example. Tabulations of the properties of water and steam (water vapor) are commonly called the **steam tables**, although the tables are as much about water as they are about steam.



Temp. °C T	Sat. press. kPa P_{sat}	Specific volume m³/kg Sat. liquid v_f	 Sat. vapor v_g
85	57.868	0.001032	2.8261
90	70.183	0.001036	2.3593
95	84.609	0.001040	1.9808

Figure 2 A partial list of Table A–4.

Example 2. Vapor pressure using steam table

Do the conditions of 25°C and 4 atm refer to liquid water, a saturated liquid vapor mixture, or water vapor?

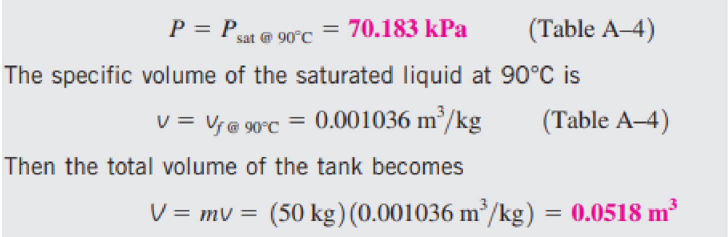
Solution

In the SI steam tables of T versus p* for saturated water, T is just less than 300 K at which p* = 3.536 kPa. Because the given pressure was about 400 kPa, much higher than the saturation pressure at 298 K, clearly the water is subcooled (compressed liquid).

Example 3. Pressure of Saturated Liquid in a Tank

A rigid tank contains 50 kg of saturated liquid water at 90°C. Determine the pressure in the tank and the volume of the tank.

Solution



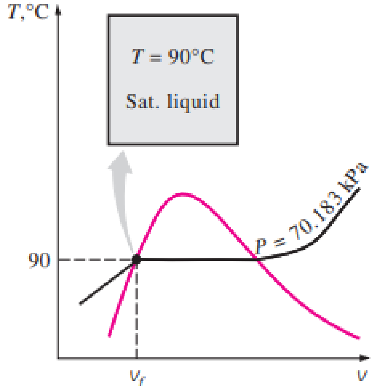
$$P = P_{\text{sat @ }90^\circ\text{C}} = \mathbf{70.183\ kPa} \qquad \text{(Table A–4)}$$

The specific volume of the saturated liquid at 90°C is

$$v = v_{f\text{ @ }90^\circ\text{C}} = 0.001036\ \text{m}^3/\text{kg} \qquad \text{(Table A–4)}$$

Then the total volume of the tank becomes

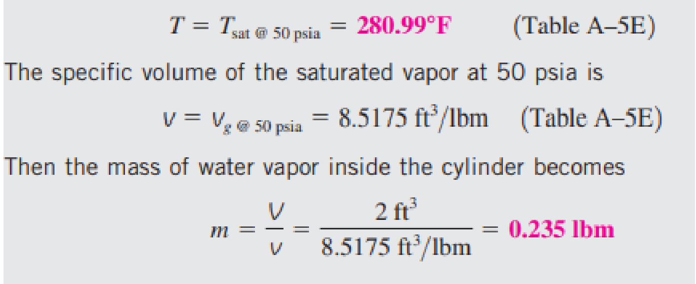
$$V = mv = (50\ \text{kg})(0.001036\ \text{m}^3/\text{kg}) = \mathbf{0.0518\ m^3}$$



Example 4. Temperature of Saturated Vapor in a Cylinder

A piston–cylinder device contains 2 ft^3 of saturated water vapor at 50-psia pressure. Determine the temperature and the mass of the vapor inside the cylinder.

Solution



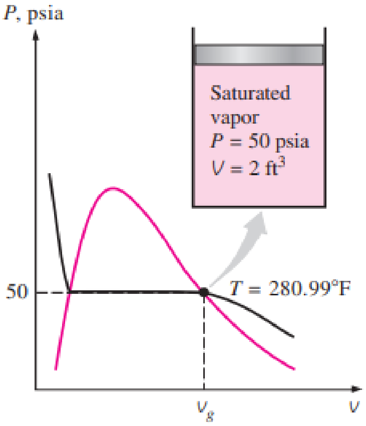
$$T = T_{\text{sat @ 50 psia}} = \mathbf{280.99^\circ F} \qquad \text{(Table A–5E)}$$

The specific volume of the saturated vapor at 50 psia is

$$v = v_{g\text{ @ 50 psia}} = 8.5175\ \text{ft}^3/\text{lbm} \qquad \text{(Table A–5E)}$$

Then the mass of water vapor inside the cylinder becomes

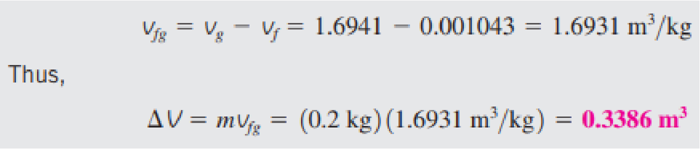
$$m = \frac{V}{v} = \frac{2\ \text{ft}^3}{8.5175\ \text{ft}^3/\text{lbm}} = \mathbf{0.235\ lbm}$$



Example 5 Volume Change during Evaporation

A mass of 200 g of saturated liquid water is completely vaporized at a constant pressure of 100 kPa. Determine the volume change.

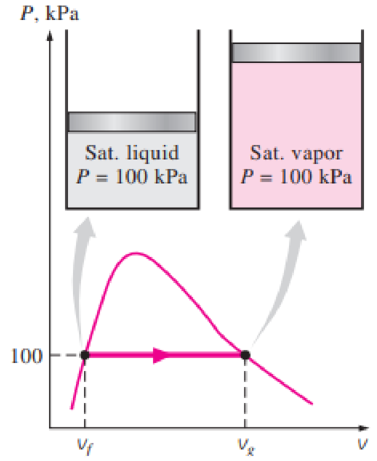
Solution



$$v_{fg} = v_g - v_f = 1.6941 - 0.001043 = 1.6931 \text{ m}^3/\text{kg}$$

Thus,

$$\Delta V = m v_{fg} = (0.2 \text{ kg})(1.6931 \text{ m}^3/\text{kg}) = 0.3386 \text{ m}^3$$



3.3 Saturated Liquid–Vapor Mixture

During a vaporization process, a substance exists as part liquid and part vapor. That is, it is a mixture of saturated liquid and saturated vapor (Figure 3). To analyze this mixture properly, we need to know the proportions of the liquid and vapor phases in the mixture. This is done by defining a new property called the ***quality x*** as the ratio of the mass of vapor to the total mass of the mixture:

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}}$$

where

$$m_{\text{total}} = m_{\text{liquid}} + m_{\text{vapor}} = m_f + m_g$$

Quality has significance for saturated mixtures only. It has no meaning in the compressed liquid or superheated vapor regions. Its value is between 0 and 1. The quality of a system that consists of saturated liquid is 0 (or 0 percent), and the quality of a system consisting of saturated vapor is 1 (or 100 percent). In saturated mixtures, quality can serve as one of the two independent intensive properties needed to describe a state. Note that the properties of the saturated liquid are the same whether it exists alone or in a mixture with saturated vapor. During the vaporization process, only the amount of saturated liquid changes, not its properties. The same can be said about a saturated vapor.

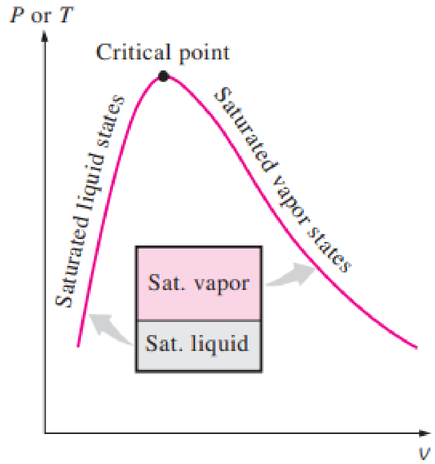
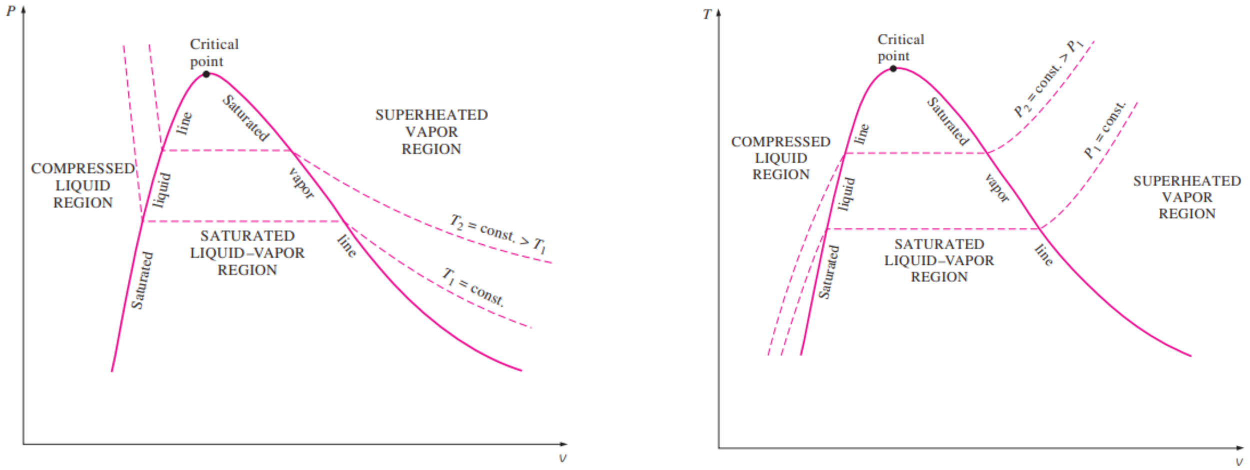


Figure 3. The relative amounts of liquid and vapor phases in a saturated mixture are specified by the ***quality x***.



P-v diagram of a pure substance.

T-v diagram of a pure substance.

Figure 4 Diagrams of T-$\hat{V}$ and P-$\hat{V}$

Consider a tank that contains a saturated liquid–vapor mixture. The volume occupied by saturated liquid is V_f, and the volume occupied by saturated vapor is V_g. The total volume V is the sum of the two:

$$V = V_f + V_g$$

$$V = mv \longrightarrow m_t v_{avg} = m_f v_f + m_g v_g$$

$$m_f = m_t - m_g \longrightarrow m_t v_{avg} = (m_t - m_g)v_f + m_g v_g$$

Dividing by m_t yields

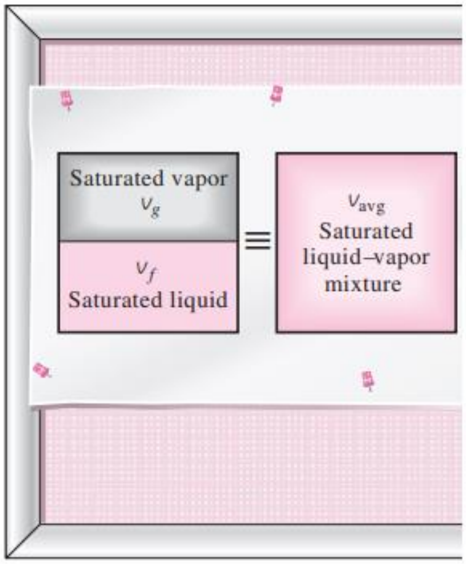
$$v_{avg} = (1 - x)v_f + xv_g$$

since $x = m_g/m_t$. This relation can also be expressed as

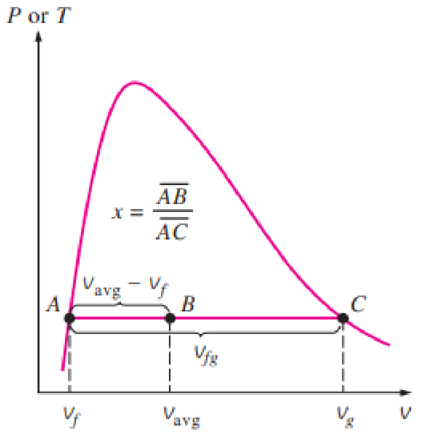
$$v_{avg} = v_f + xv_{fg} \qquad (\mathrm{m^3/kg})$$

where $v_{fg} = v_g - v_f$. Solving for quality, we obtain

$$x = \frac{v_{avg} - v_f}{v_{fg}}$$



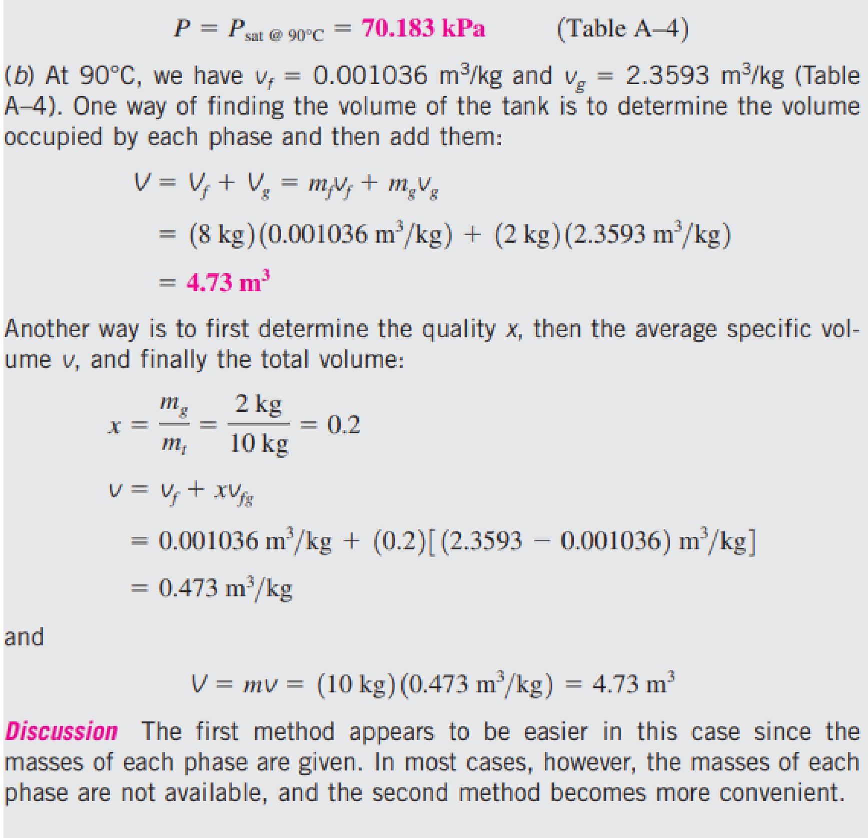
Based on this equation, quality can be related to the horizontal distances on a P-v or T-v diagram (Figure 5). At a given temperature or pressure, the numerator of Eq. 3–5 is the distance between the actual state and the saturated liquid state, and the denominator is the length of the entire horizontal line that connects the saturated liquid and saturated vapor states. A state of 50 percent quality lies in the middle of this horizontal line.



Example 6. Pressure and Volume of a Saturated Mixture

A rigid tank contains 10 kg of water at 90°C. If 8 kg of the water is in the liquid form and the rest is in the vapor form, determine (a) the pressure in the tank and (b) the volume of the tank.

Solution



$$P = P_{sat\,@\,90°C} = \mathbf{70.183\ kPa} \qquad \text{(Table A–4)}$$

(*b*) At 90°C, we have $v_f = 0.001036\ m^3/kg$ and $v_g = 2.3593\ m^3/kg$ (Table A–4). One way of finding the volume of the tank is to determine the volume occupied by each phase and then add them:

$$\begin{aligned} V &= V_f + V_g = m_f v_f + m_g v_g \\ &= (8\ kg)(0.001036\ m^3/kg) + (2\ kg)(2.3593\ m^3/kg) \\ &= \mathbf{4.73\ m^3} \end{aligned}$$

Another way is to first determine the quality x, then the average specific volume v, and finally the total volume:

$$x = \frac{m_g}{m_t} = \frac{2\ kg}{10\ kg} = 0.2$$

$$\begin{aligned} v &= v_f + x v_{fg} \\ &= 0.001036\ m^3/kg + (0.2)[(2.3593 - 0.001036)\ m^3/kg] \\ &= 0.473\ m^3/kg \end{aligned}$$

and

$$V = mv = (10\ kg)(0.473\ m^3/kg) = 4.73\ m^3$$

Discussion The first method appears to be easier in this case since the masses of each phase are given. In most cases, however, the masses of each phase are not available, and the second method becomes more convenient.

Example 7. Interpolating in the Steam Tables

What is the saturation pressure of water at 312 K (39 ^{0}C)?

Solution

To solve this problem, you have to carry out a single interpolation. Look in the steam tables under the properties of saturated water to get *p** so as to bracket 39 ^{0}C:

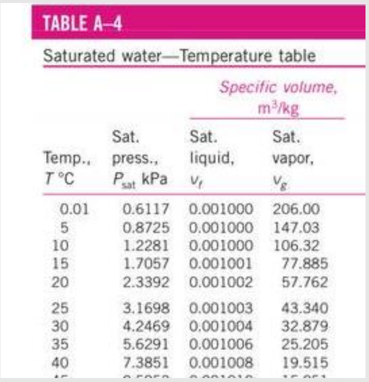


TABLE A–4

Saturated water—Temperature table

		Specific volume, m^3/kg	
Temp., T °C	Sat. press., P_{sat} kPa	Sat. liquid, v_f	Sat. vapor, v_g
0.01	0.6117	0.001000	206.00
5	0.8725	0.001000	147.03
10	1.2281	0.001000	106.32
15	1.7057	0.001001	77.885
20	2.3392	0.001002	57.762
25	3.1698	0.001003	43.340
30	4.2469	0.001004	32.879
35	5.6291	0.001006	25.205
40	7.3851	0.001008	19.515

$$y - y_1 = \frac{y_2 - y_1}{x_2 - x_1}(x - x_1)$$

T (^{0}C)	p*(Kpa)
35	5.6291
39	–
40	7.3851

$$p^* = 5.6291 + \frac{(7.3851 - 5.6291)}{(40 - 35)} \times (39 - 35) = 7.0339 Kpa$$

Homework: An 80-L vessel contains 4 kg of refrigerant-134a at a pressure of 160 kPa. Determine (a) the temperature, (b) the quality, and (c) the volume occupied by the vapor phase.

4. Two-Component Gas/Single-Component Liquid Systems

A system with two components in the gas phase together with a single component liquid system. An example of such a system is water and a non-condensable gas, such as air. The equilibrium relationships for the water and air help explain how rain is formed and lead to several meteorological terms, such as the ***dew point*** and the ***humidity*** of the air. Moreover, the equilibrium relationship for two-component gas/single-component liquid systems is used industrially to describe and design many systems, including cooling towers, in which water is cooled by evaporation, and stripping systems, in which a volatile component is removed from a liquid by contacting the liquid with a non-condensable gas.

4.1 Saturation

When any non-condensable gas (or a gaseous mixture) comes in contact with a liquid, the gas will acquire molecules from the liquid. If contact is maintained for a sufficient period, vaporization continues until equilibrium is attained, at which time ***the partial pressure of the vapor in the gas will equal the vapor pressure of the liquid at the temperature of the system.*** Regardless of the duration of contact between the liquid and gas, after equilibrium is reached, no more net liquid will vaporize into the gas phase. The gas is then said to be **saturated** with the particular vapor at the given temperature. We also say that the gas mixture is at its dew point. The **dew point** for the mixture of pure vapor and non-condensable gas means the temperature at which the vapor would just start to condense if the temperature were very slightly reduced. At the dew point, the partial pressure of the vapor is equal to the vapor pressure of the volatile liquid.

A a gas is saturated, you can determine the composition of the vapor-gas mixture from knowledge of the vapor pressure of the vapor (or the temperature of the saturated mixture) to use in material balances. The ideal gas law applies to both air and water vapor at atmospheric pressure with excellent precision. Thus, the following relations hold *at saturation:*

$$\frac{p_{H_2O}V}{p_{air}V} = \frac{n_{H_2O}RT}{n_{air}RT}$$

or

$$\frac{p_{H_2O}}{p_{air}} = \frac{p^*_{H_2O}}{p_{air}} = \frac{n_{H_2O}}{n_{air}} = \frac{p_{total} - p_{air}}{p_{air}}$$

because V and T are the same for the air and water vapor.

Also,

$$y_{H_2O} = \frac{p_{H_2O}}{p_{total}} = \frac{p_{H_2O}}{p_{air} + p_{H_2O}} = 1 - y_{air}$$

Example 8. Saturated gas (air and water)

Suppose you have a saturated gas, say, water in air at 51°C, and the pressure on the system is 750 mm Hg absolute. What is the partial pressure of the air?

Solution

If the air is saturated, you know that the partial pressure of the water vapor is *p** at 51°C. use the steam tables, and find that *p** using interpolation and equal to 97.7645 mmHg.

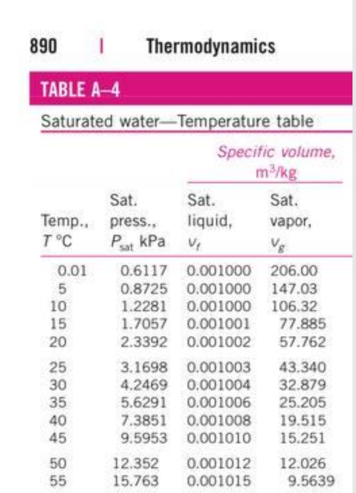


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TABLE A–4

Saturated water—Temperature table

Temp., T °C	Sat. press., P_{sat} kPa	Specific volume, m³/kg Sat. liquid, v_f	 Sat. vapor, v_g
0.01	0.6117	0.001000	206.00
5	0.8725	0.001000	147.03
10	1.2281	0.001000	106.32
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25	3.1698	0.001003	43.340
30	4.2469	0.001004	32.879
35	5.6291	0.001006	25.205
40	7.3851	0.001008	19.515
45	9.5953	0.001010	15.251
50	12.352	0.001012	12.026
55	15.763	0.001015	9.5639

$$p^*_{H_2O} = 12.352 + \frac{15.763 - 12.352}{55 - 50} \times (51 - 50) = 13.0342 \text{Kpa} \ \ (97.7645 \ \ \text{mmHg})$$

$$p_{air} = 750 - 97.7645 = 652.2355 \text{Kpa}$$

$$\text{y}_{air} = \frac{652.2355}{750} = 0.87$$

$$y_{H_2O} = 1 - 0.87 = 0.13$$

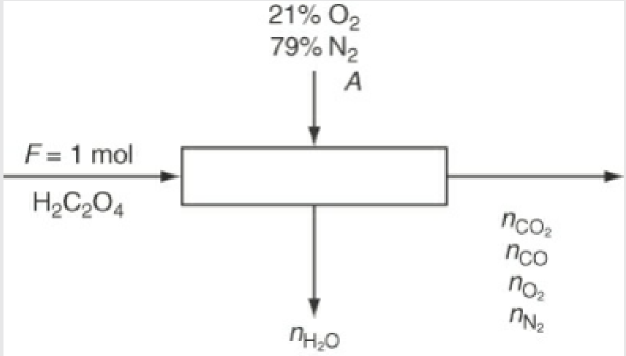
Example 9: Calculation of the Dew Point of the Products of Combustion

Oxalic acid ($H_2C_2O_4$) is burned at atmospheric pressure with 4% excess air so that 65% of the carbon burns to CO. Calculate the dew point of the product gas.

Solution

The solution of the problem involves the following steps:

1. Calculate the combustion products via material balances.
2. Calculate the mole fraction of the water vapor in the combustion products as indicated just prior to this example.
3. Assume a total pressure, say, 1 atm, and calculate $y_{H_2O}\, p_{total} = p_{H_2O}$ in the combustion products. At equilibrium p_{H_2O} will be the vapor pressure $p^*_{H_2O}$.
4. Condensation (at constant total pressure) would be possible when $p^*_{H_2O}$ equals the calculated p_{H_2O}. This value is the dew point.
5. Look up the temperature corresponding to p_{H_2O} in the saturated steam tables.



Steps 1–5

Basis: 1 mol of $H_2C_2O_4$

The figure and data are given. The chemical reaction equation for the combustion of oxalic acid is given as

$$H_2C_2O_4 + 0.5O_2 \rightarrow 2CO_2 + H_2O$$
$$H_2C_2O_4 \rightarrow 2CO + H_2O + 0.5O_2$$

Step 4

O_2 required:

$$\frac{1\,\text{mol}\,H_2C_2O_4}{1}\;\frac{0.5\,\text{mol}\,O_2}{1\,\text{mol}\,H_2C_2O_4} = 0.5\,\text{mol}\,O_2\,(\text{note oxygen in oxalic acid})$$

Moles of O_2 in with air including excess:

$$(1 + 0.04)\,(0.5 \text{ mol } O_2) = 0.52 \text{ mol } O_2$$

Therefore, 0.52/0.21 = 2.48 mol air enters containing 1.96 mol n_{N_2}.

Specifications: 65% of the carbon burns to CO: (0.65) (2) = 1.30.

The results:

Element Material Balances

Element	In (mol)	Out (mol)
C	2	$n_{CO_2} + n_{CO}$ or $0.70 + 1.30$
H	2	$2n_{H_2O}$
N	1.96 × 2	1.96 × 2
O	0.52 × 2 + 4	$2n_{CO_2} + n_{CO} + n_{O_2}$ or $2(0.70) + 1.30 + 1.0 + 2n_{O_2}$

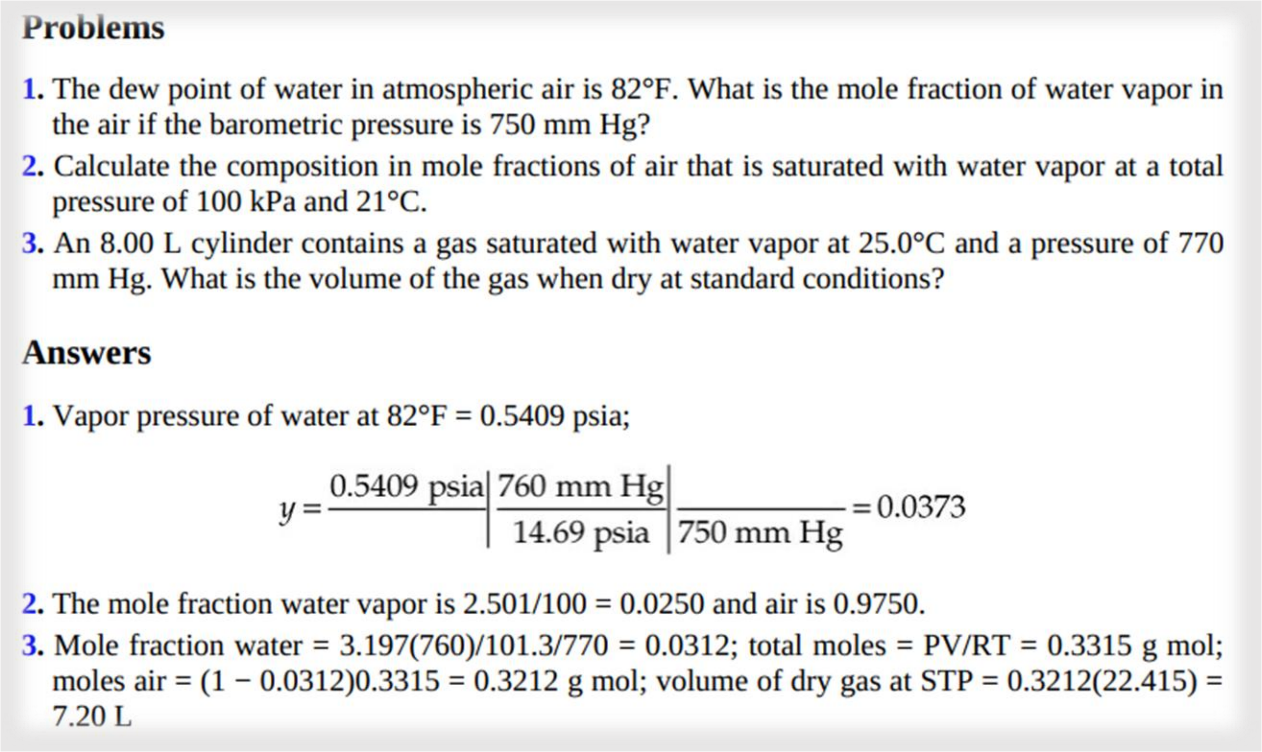
$$n_{H_2O} = 1.0;\ n_{CO_2} = 0.7;\ n_{CO} = 1.3;\ n_{O_2} = 0.67;\ n_{N_2} = 1.96;\ \text{total mol} = 5.63$$

$$y_{H_2O} = 1 \text{ mol } H_2O/6.78 \text{ mol} = 0.178$$

The partial pressure of the water in the product gas (at an assumed atmospheric pressure) determines the dew point of the stack gas; that is, the temperature of saturated steam that equals the partial pressure of the water is equal to the dew point of the product gas:

$$p^{*}_{H_2O} = y_{H_2O}(p_{\text{total}}) = 0.178(101.3\,\text{kPa}) = 18.0\,\text{kPa}\,(\text{i.e., } 2.61\,\text{psia})$$

From the steam tables, T = 136°F.



Problems

1. The dew point of water in atmospheric air is 82°F. What is the mole fraction of water vapor in the air if the barometric pressure is 750 mm Hg?
2. Calculate the composition in mole fractions of air that is saturated with water vapor at a total pressure of 100 kPa and 21°C.
3. An 8.00 L cylinder contains a gas saturated with water vapor at 25.0°C and a pressure of 770 mm Hg. What is the volume of the gas when dry at standard conditions?

Answers

1. Vapor pressure of water at 82°F = 0.5409 psia;

$$y = \frac{0.5409 \text{ psia}}{} \left| \frac{760 \text{ mm Hg}}{14.69 \text{ psia}} \right| \frac{}{750 \text{ mm Hg}} = 0.0373$$

2. The mole fraction water vapor is 2.501/100 = 0.0250 and air is 0.9750.
3. Mole fraction water = 3.197(760)/101.3/770 = 0.0312; total moles = PV/RT = 0.3315 g mol; moles air = (1 − 0.0312)0.3315 = 0.3212 g mol; volume of dry gas at STP = 0.3212(22.415) = 7.20 L

4.2 Condensation

Condensation is the change of vapor in a non-condensable gas to liquid. Some typical ways of condensing a vapor that is in a gas are to

1. Cool it at constant total system pressure (the volume changes)
2. Cool it at constant total system volume (the pressure changes)
3. Compress it isothermally (the volume changes)

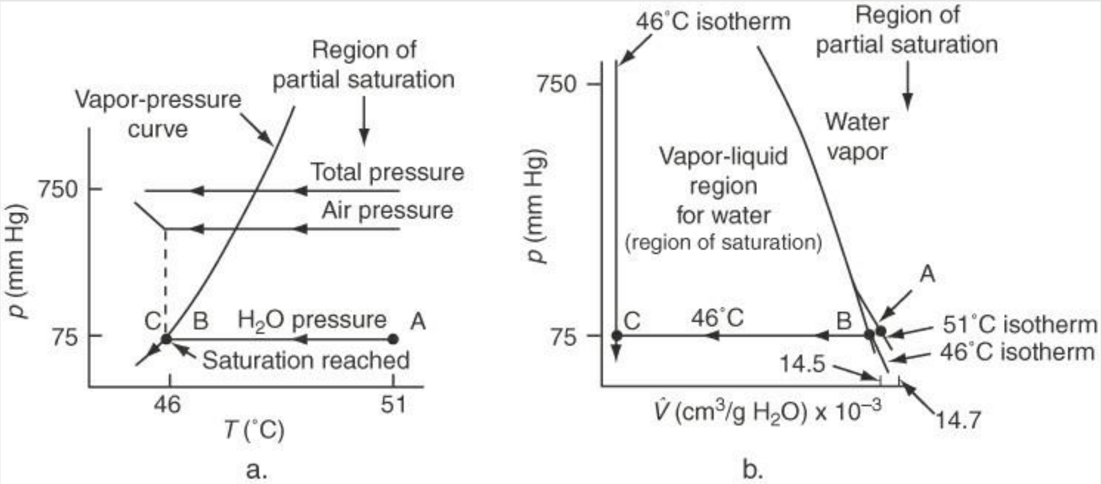
Example 10: Condensation at constant pressure

The cooling at constant total system pressure for a mixture of air and 10% water vapor. Pick the air-water vapor mixture as the system. If the mixture is cooled at constant total pressure from 51°C and 750 mm Hg absolute (point A in Figures below a and b for the water), how low can the temperature go before condensation starts (at point B)?

Solution

The cooling of the mixture until the temperature reaches the dew point associated with the partial pressure of water of

$$p^*_{H_2O} \equiv p_{H_2O} = 0.10(750) = 75\ \text{mm Hg}$$



a.

b.

From the steam tables, you can find that the corresponding temperature is T = 46°C (point B on the vapor curve). After reaching p^* = 75 mm Hg at point B, if the condensation process continues, it continues at constant pressure (75 mm Hg) and constant temperature (46°C) until all of the water vapor has been condensed to liquid (point C). Further cooling will reduce the temperature of the liquid water below 46°C.

Condensation can also occur when the pressure on a vapor-gas mixture is increased.

Example 10: Condensation at the pressure on a vapor-gas mixture is increased

A pound of saturated air at 75°F is isothermally compressed, liquid water will be condensed out of the air. If a pound of saturated air at 75°F and 1 atm (the vapor pressure of water is 0.43 psia at 75°F) is compressed isothermally to 4 atm. Remove the liquid water, expand the air isothermally back to 1 atm, Find the dew point for finally stage.

Solution

A pound of saturated air at 75°F is isothermally compressed (with a reduction in volume, of course), liquid water will be condensed out of the air (see Figure 5). If a pound of saturated air at 75°F and 1 atm (the vapor pressure of water is 0.43 psia at 75°F) is compressed isothermally to 4 atm (58.8 psia), almost three-fourths of the original content of water vapor now will be in the form of liquid, and the air still has a dew point of 75°F. Remove the liquid water, expand the air isothermally back to 1 atm, and you will find that the dew point has been lowered to about 36°F.

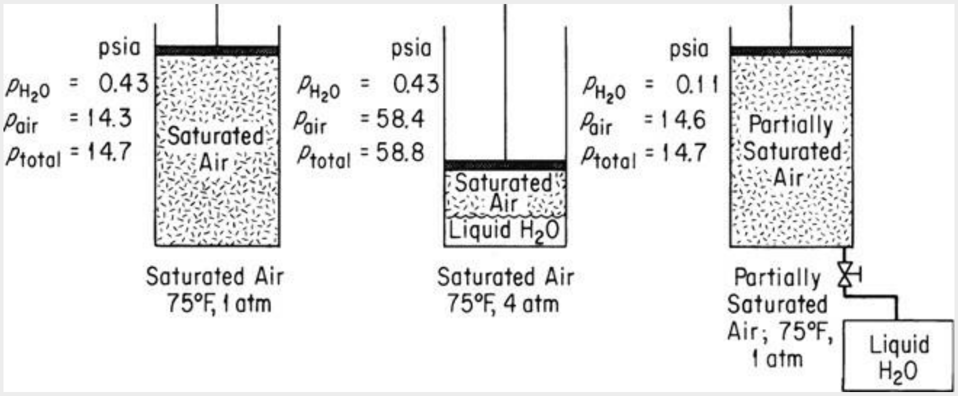


Figure 5: Effect of an increase of pressure on saturated air, removal of condensed water, and a return to the initial pressure at constant temperature

Mathematically (1 = state at 1 atm, 4 = state at 4 atm), with *z* = 1.00 for both components:

For the same air saturated at 75°F and 1 atm:

$$\left(\frac{n_{H_2O}}{n_{air}}\right)_1 = \left(\frac{p^*_{H_2O}}{p_{air}}\right)_1 = \frac{0.43}{14.3}$$

For saturated air at 75°F and 4 atm:

$$\left(\frac{n_{H_2O}}{n_{air}}\right)_4 = \left(\frac{p^*_{H_2O}}{p_{air}}\right)_4 = \frac{0.43}{58.4}$$

The material balance gives for the H2O:

$$\left(\frac{n_4}{n_1}\right)_{H_2O} = \frac{\frac{0.43}{58.4}}{\frac{0.43}{14.3}} = \frac{14.3}{58.4} = 0.245$$

In other words, 24.5% of the original water will remain as vapor after compression.

After the air-water vapor mixture is returned to a total pressure of 1 atm, the following two equations now apply at 75°F:

$$p_{H_2O} + p_{air} = 14.7$$

$$\frac{p_{H_2O}}{p_{air}} = \frac{n_{H_2O}}{n_{air}} = \frac{0.43(0.245)}{14.3} = 0.00737$$

From these two relations you can find that:

$$\begin{aligned} p_{H_2O} &= 0.108 \text{ psia} \\ p_{air} &= \underline{14.6 \text{ psia}} \\ p_{air} &= 14.7 \text{ psia} \end{aligned}$$

This pressure of the water vapor represents a dew point of about 36°F

Example 11: Explain how the pressure for a pure component change (higher, lower, no change) for the following scenarios:

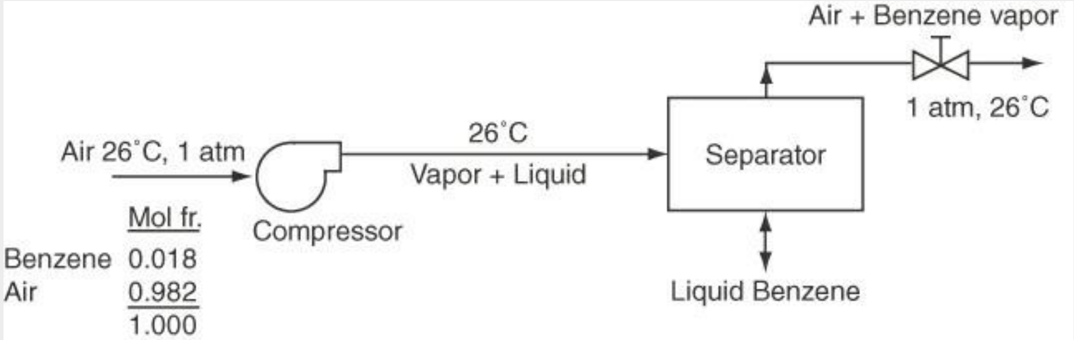
a. A system containing saturated liquid is compressed at constant temperature.
b. A system containing saturated liquid is expanded at constant temperature.
c. A system containing saturated liquid is heated at constant volume.
d. A system containing saturated liquid is cooled at constant volume.
e. A system containing saturated vapor is compressed at a constant temperature.
f. A system containing saturated vapor is expanded at a constant temperature.
g. A system containing saturated vapor is heated at constant volume.
h. A system containing saturated vapor is cooled at constant volume.
i. A system containing vapor and liquid in equilibrium is heated at constant volume.
j. A system containing vapor and liquid in equilibrium is cooled at constant volume.
k. A system containing a superheated gas is expanded at a constant temperature.
l. A system containing superheated gas is compressed at a constant temperature

Solution:

(a) higher; (b) lower; (c) higher; (d) lower; (e) no change; (f) lower; (g) higher; (h) lower; (i) higher; (j) lower; (k) lower; (l) higher

Example 12: Condensation of Benzene from a Vapor Recovery Unit

The removal of benzene vapor from an exhaust stream, shown in Figure below, designed to recover 95% of the benzene from air by compression. What is the exit pressure from the compressor? If the vapor pressure of benzene at 26°C is *p** = 99.7 mm Hg.



Solution

a short material balance to determine the outlet concentrations from the compressor:
Basis: 1 g mol of entering gas at 26°C and 1 atm
Entering components to the compressor:

$$\begin{aligned} \text{mol of benzene} &= 0.018(1) = 0.018 \text{ g mol} \\ \text{mol of air} &= 0.982(1) = \underline{0.982} \text{ g mol} \\ \text{total gas} &= 1.000 \text{ g mol} \end{aligned}$$

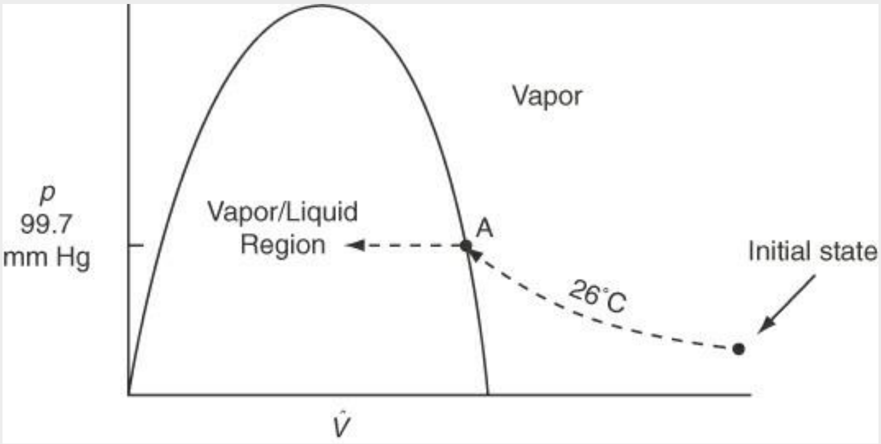
Exiting components in the gas phase from the compressor:

$$\begin{aligned} \text{mol of benzene} &= 0.018(0.05) = 0.90\times10^{-3} \text{ g mol} \\ \text{mol of air} &= \underline{0.982} \text{ g mol} \\ \text{total gas} &= 0.983 \text{ g mol} \\ y_{\text{Benzene exiting}} &= \frac{0.90\times10^{-3}}{0.983} = 0.916\times10^{-3} = \frac{p_{\text{Benzene}}}{p_{\text{total}}} \end{aligned}$$

Now the partial pressure of the benzene is 99.7 mm Hg, so

$$p_{\text{total}} = \frac{99.7 \text{ mm Hg}}{0.916\times10^{-3}} = 108\times10^{3} \text{ mm Hg} \,(143 \text{ atm})$$

Could you increase the pressure at the exit of the pump above 143 atm? Only if all of the benzene vapor condenses to liquid. Imagine that the dashed line in Figure below is extended to the left until it reaches the saturated liquid line (bubble point line). Subsequently, the pressure can be increased on the liquid (it would follow a vertical line as liquid benzene is not very compressible).



Homework

1. A mixture of air and benzene contains 10 mol % benzene at 43°C and 105 kPa pressure. At what temperature can the first liquid form? What is the liquid?

2. Two hundred pounds of water out of 1000 lb is electrolytically decomposed into hydrogen and oxygen at 25°C and 740 mm Hg absolute. The hydrogen and oxygen are separated at 740 mm Hg and stored in two different cylinders, each at 25°C and a pressure of 5.0 atm absolute. How much water condenses from the gas in each cylinder?

4.3 Vaporization

At equilibrium, you can vaporize a liquid into a non-condensable gas and raise the partial pressure of the vapor in the gas until the saturation pressure (vapor pressure) is reached. Figure 5 shows how the partial pressures of water and air change with time as water evaporates into dry air. On a *p*-*T* diagram such as Figure 7.2, the liquid would vaporize at the saturation temperature on line AB in the figure (the bubble point temperature which is equal to the dew point temperature) until the air was saturated

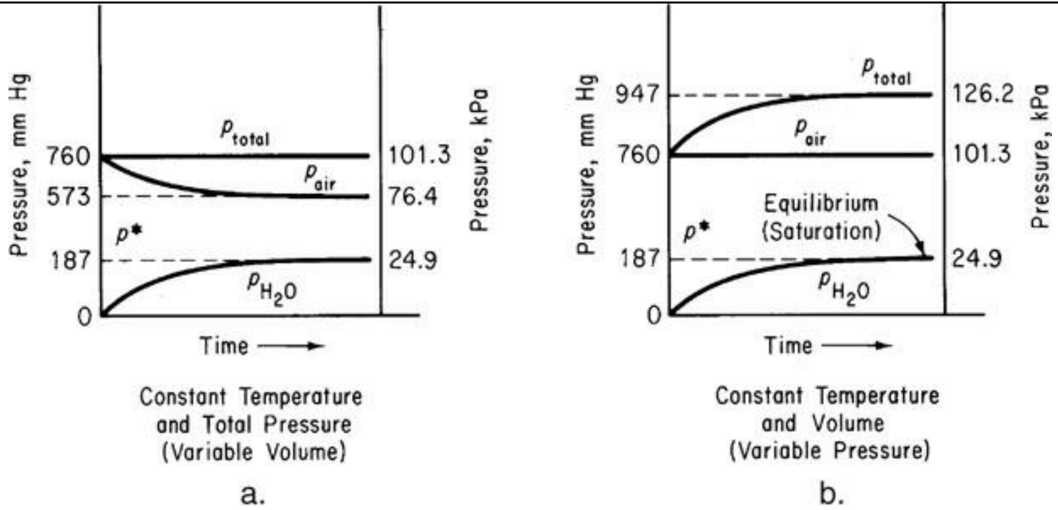


Figure 6 Change of partial and total pressure during the vaporization of water into initially dry air (a) at constant temperature and total pressure (variable volume); (b) at constant temperature and volume (variable pressure)

At constant total pressure, as shown in Figure 7, the volume of the air would remain constant, but the volume of water vapor would increase, so a total volume of the mixture would increase.

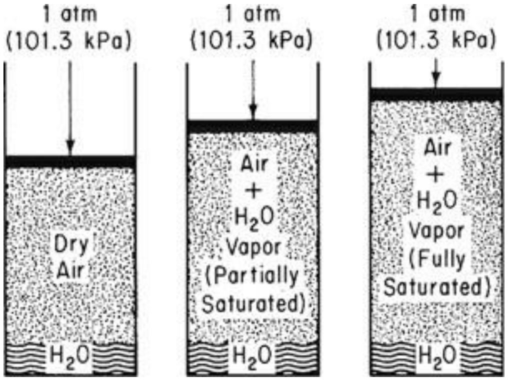


Figure 7 Evaporation of water at constant pressure and temperature of 65°C

Example 13: vaporization

If sufficient liquid water is placed in a volume of dry gas that is at 15°C and 754 mm Hg, and if the temperature and volume remain constant during the vaporization, what is the final pressure in the system?

Solution

The partial pressure of the dry gas remains constant because *n, V,* and *T* for the dry gas are constant. The water vapor reaches its vapor pressure of 12.8 mm Hg at 15°C from steam table. Thus, the total pressure is:

$$p_{\text{tot}} = p_{\text{H}_2\text{O}} + p_{\text{air}} = 12.8 + 754 = 766.8 \text{ mm Hg}$$

Example 14 Vaporization to Saturate Dry Air

Problem Statement

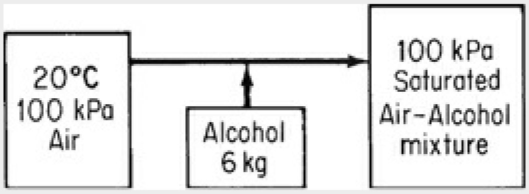
What is the minimum number of cubic meters of dry air at 20°C and 100 kPa that are necessary to evaporate 6.0 kg of ethyl alcohol (46.07 kg/kmol) if the total pressure remains constant at 100 kPa and the temperature remains 20°C? Assume that the air is blown through the alcohol to evaporate it in such a way that the exit pressure of the air-alcohol mixture is at 100 kPa.

Solution

The process is isothermal. The additional data needed are:

T	293
A	18.5242
B	3578.91
C	-50.5
C+T	242.5
B/C+T	14.76
A-B/C+T	3.77
ln (p)	3.77
p mmHg	43.2
p Kpa	5.76

$$p^{*}_{\text{alcohol}} \text{ at } 20°\text{C} = 5.93 \text{ kPa}$$



The minimum volume of air means that the resulting mixture is saturated; any condition less than saturated would require more air.

Basis: 6.0 kg of alcohol

The ratio of moles of ethyl alcohol to moles of air in the final gaseous mixture is the same as the ratio of the partial pressures of these two substances. Since we know the moles of alcohol, we can find the number of moles of air needed for the vaporization.

$$\frac{p^*_{\text{alcohol}}}{p_{\text{air}}} = \frac{n_{\text{alcohol}}}{n_{\text{air}}}$$

Once you calculate the number of moles of air, you can apply the ideal gas law. Since $p^*_{\text{alcohol}} = 5.93\,\text{kPa}$

$$p_{\text{air}} = p_{\text{total}} - p^*_{\text{alcohol}} = (100 - 5.93)\,\text{kPa} = 94.07\,\text{kPa}$$

$$\frac{6.0 \text{ kg alcohol}}{} \left| \frac{1 \text{ kg mol alcohol}}{46.07 \text{ kg alcohol}} \right| \frac{94.07 \text{ kg mol air}}{5.93 \text{ kg mol alcohol}} = 2.07 \text{ kg mol air}$$

$$V_{\text{air}} = \frac{2.07 \text{ kg mol air}}{} \left| \frac{8.314 (\text{kPa})(\text{m}^3)}{(\text{kg mol})\ (\text{K})} \right| \frac{293 \text{ K}}{100 \text{ kP}} = 50.3 \text{ m}^3 \text{ at } 20^\circ\text{C and 100 kPa}$$

Questions

1. If a dry gas is isothermally mixed with a liquid in a fixed volume, will the pressure remain constant with time?

2. If dry gas is placed in contact with a liquid phase under conditions of constant pressure and allowed to come to equilibrium:

a. Will the total pressure increase with time?

b. Will the volume of the gas plus liquid plus vapor increase with time?

c. Will the temperature increase with time?

Answers

1. No, it will increase slightly.

2. (a) No; (b) Yes; (c) No

Problems

1. Phase Diagrams and the Phase Rule

a) What is the number of degrees of freedom according to the phase rule for each of the following systems: (a) solid iodine in equilibrium with its vapor; (b) a mixture of liquid water and liquid octane (which is immiscible in water), both in equilibrium with their vapors?

b) In the decomposition of CaCO3 in a sealed container from which the air was initially pumped out, you generate CO_2 and CaO. If not all of the $CaCO_3$ decomposes at equilibrium, how many degrees of freedom exist for the system according to the Gibbs phase rule?

2. Single-Component Two-Phase Systems (Vapor Pressure)

a) Calculate the vapor pressure of each compound listed below at the designated temperature using the Antoine equation and the coefficients in Appendix G. Compare your results with the corresponding values of the vapor pressures obtained from the Antoine equation found in the physical properties package on the CD accompanying this book.

a. Acetone at 0°C.
b. Benzene at 80°F.
Carbon tetrachloride at 300 K.

b) A vessel that has a volume of 0.35 m3 contains 2 kg of a mixture of liquid water and water vapor at equilibrium with a pressure of 450 kPa. What is the quality of the water vapor?

c) A vessel with an unknown volume is filled with 10 kg of water at 90°C. Inspection of the vessel at equilibrium shows that 8 kg of the water is in the liquid state. What is the pressure in the vessel, and what is the volume of the vessel?

d) In a vessel with a volume of 3.00 m^3, you put 0.030 m3 of liquid water and 2.97 m^3 of water vapor so that the pressure is 101.33 kPa. Then you heat the system until all of the liquid water just evaporates. What are the temperature and pressure in the vessel at that time?

3. Two-Component Gas/Single-Component Liquid Systems

a) A large chamber contains dry N_2 at 27°C and 101.3 kPa. Water is injected into the chamber. After saturation of the N_2 with water vapor, the temperature in the chamber is 27°C.

a. What is the pressure inside the chamber after saturation?
b. How many moles of H_2O per mole of N_2 are present in the saturated mixture?

b) A mixture of acetylene (C_2H_2) with an excess of oxygen measured 350 ft^3 at 25°C and 745 mm Hg absolute pressure. After the explosion the volume of the dry gaseous product was 300 ft^3 at 60°C and the same pressure. Calculate the volume of acetylene and oxygen in the original mixture. The final gas was saturated. Assume that all of the water resulting from the reaction was in the gas phase after the reaction.

c) CH_4 is completely burned with air. The outlet gases from the burner, which contain no oxygen, are passed through an absorber where some of the water is removed by condensation. The gases leaving the absorber have a nitrogen mole fraction of 0.8335. If the exit gases from the absorber are at 130°F and 20 psia:

a. To what temperature must this gas be cooled at constant pressure in order to start condensing more water?
b. To what pressure must this gas be compressed at constant temperature before more
condensation will occur?

d) One thousand cubic meters of air saturated with water vapor at 30°C and 99.0 kPa is cooled to 14°C and compressed to 133 kPa. How many kilograms of H_2O condense out?

e) Air at 25°C and 100 kPa has a dew point of 16°C. If you want to remove 50% of the initial moisture in the air (at a constant pressure of 100 kPa), to what temperature should you cool the air?

f) In a dry-cleaning establishment warm dry air is blown through a revolving drum in which clothes are tumbled until all of the Stoddard solvent is removed. The solvent may be assumed to be n-octane (C_8H_{18}) and have a vapor pressure of 2.36 in. Hg at 120°F. If the air at 120°F becomes saturated with octane, calculate (a) the pounds of air required to evaporate 1 lb of octane, (b) the percent octane by volume in the gases leaving the drum, and (c) the cubic feet of inlet air required per pound of octane. The barometer reads 29.66 in. Hg.