Other values for R

1 atm.=1.0133*10^{6} dyn.cm^{-2}

R=1.0133*10^{6} dyn.cm^{-2} *22414 cm^{3}.mol^{-1}/273.15 ^{0}K

= 8.314*10^{7} erg.mol^{-1} ^{0}K $^{-1}$

= ***8.314 J.mol^{-1}.^{0}K^{-1}***

1 Cal = 4.18J

R= 8.314 J.mol^{-1}.^{0}K^{-1}/4.18 = ***1.987 Cal.mol^{-1}. ^{0}K^{-1}***

Example 2-2

Calculation of Volume Using the Ideal Gas Law

What is the volume of 2 moles of an ideal gas at 25°C and 780 mm Hg?

$$(780 \text{ mm}/760 \text{ mm atm}^{-1}) \times V$$
$$= 2 \text{ moles} \times (0.08205 \text{ liter atm/mole deg}) \times 298 \text{ K}$$
$$V = 47.65 \text{ liters}$$

Molecular Weight

The approximate molecular weight of a gas can be determined by use of the ideal gas law. The number of moles of gas n is

replaced by its equivalent g/M, in which g is the number of grams of gas and M is the molecular weight:

$$PV = \frac{g}{M}RT \qquad (2\text{–}7)$$

or

$$M = \frac{gRT}{PV} \qquad (2\text{–}8)$$

Example 2-3

Molecular Weight Determination by the Ideal Gas Law

If 0.30 g of ethyl alcohol in the vapor state occupies 200 mL at a pressure of 1 atm and a temperature of 100°C, what is the molecular weight of ethyl alcohol? Assume that the vapor behaves as an ideal gas. Write

$$M = \frac{0.30 \times 0.082 \times 373}{1 \times 0.2}$$
$$M = 46.0 \text{ g/mole}$$

The two methods most commonly used to determine the molecular weight of easily vaporized liquids

B- Real gas

They are composed of molecules of a finite volume tend to attract one another.

These factors affect the volume and pressure terms in the *Ideal gas equation* of state.

for n moles of real gas

$(P+an^2/v^2)\ (V-nb) = nRT$

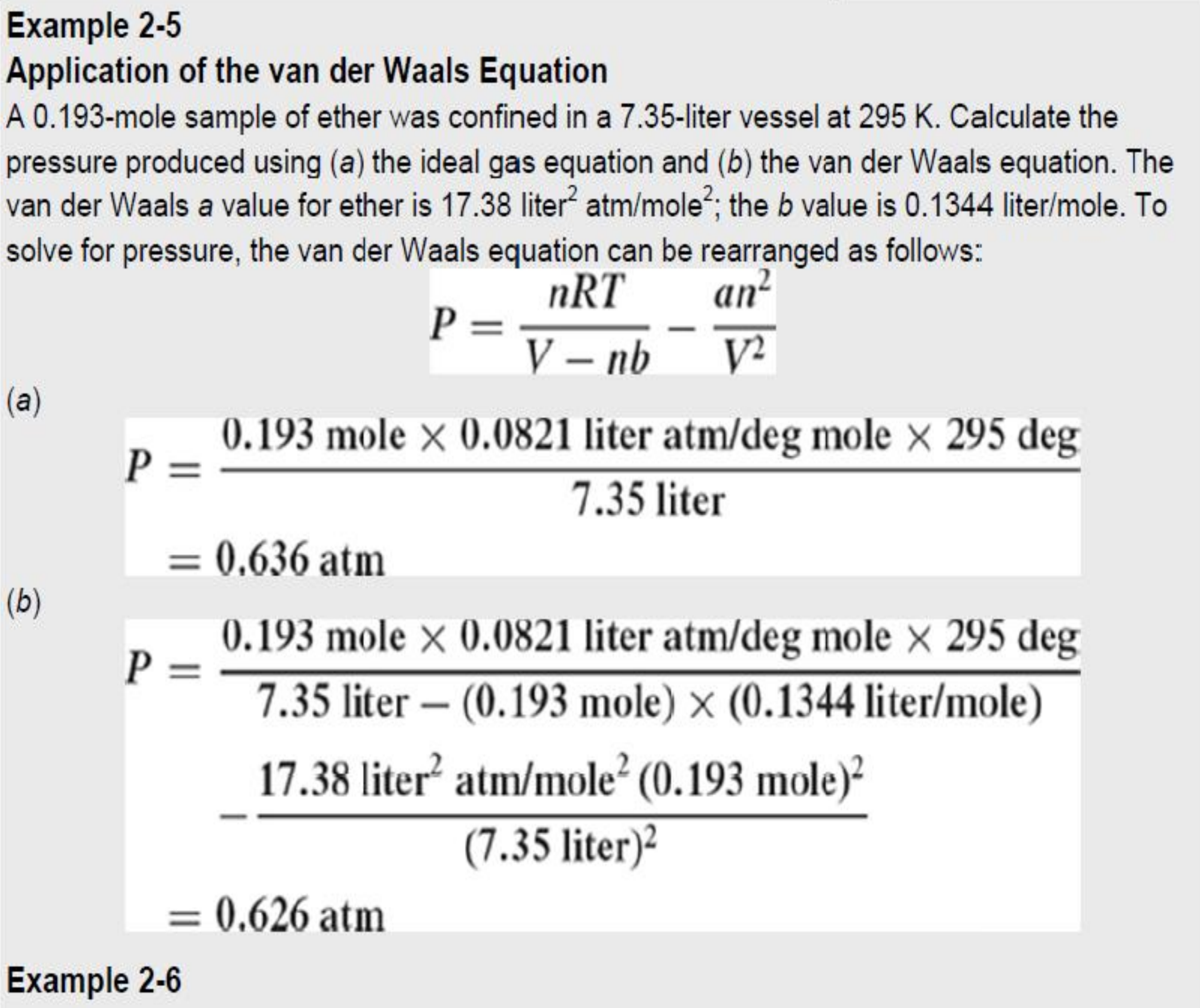
a: for pressure resulting from mole of interaction ($L^2.atm.mol^{-2}$)

b: the volume of mole molecules

$a = 27R^2Tc^2/64Pc$, $b = RTc/8Pc$

Pc, Tc: critical pressure and temperature

gas	*a*	*b*
H_2	0.244	0.0266
O_2	1.36	0.0318
CH_4	2.253	0.0428
H_2O	5.464	0.0305
$HCCl_3$	15.17	0.1022



Example 2-5

Application of the van der Waals Equation

A 0.193-mole sample of ether was confined in a 7.35-liter vessel at 295 K. Calculate the pressure produced using (*a*) the ideal gas equation and (*b*) the van der Waals equation. The van der Waals *a* value for ether is 17.38 liter^2 atm/mole^2; the *b* value is 0.1344 liter/mole. To solve for pressure, the van der Waals equation can be rearranged as follows:

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

(*a*)

$$\begin{aligned} P &= \frac{0.193 \text{ mole} \times 0.0821 \text{ liter atm/deg mole} \times 295 \text{ deg}}{7.35 \text{ liter}} \\ &= 0.636 \text{ atm} \end{aligned}$$

(*b*)

$$\begin{aligned} P &= \frac{0.193 \text{ mole} \times 0.0821 \text{ liter atm/deg mole} \times 295 \text{ deg}}{7.35 \text{ liter} - (0.193 \text{ mole}) \times (0.1344 \text{ liter/mole})} \\ &\quad - \frac{17.38 \text{ liter}^2 \text{ atm/mole}^2 (0.193 \text{ mole})^2}{(7.35 \text{ liter})^2} \\ &= 0.626 \text{ atm} \end{aligned}$$

Example 2-6

Example 2-6

Calculation of the van der Waals Constants

Calculate the pressure of 0.5 mole of CO_2 gas in a fire extinguisher of 1-liter capacity at 27°C using the ideal gas equation and the van der Waals equation. The van der Waals constants can be calculated from the critical temperature T_c and the critical pressure P_c (see the section Liquefaction of Gases for definitions):

$$a = \frac{27R^2T_c^{\,2}}{64P_c} \quad \text{and} \quad b = \frac{RT_c}{8P_c}$$

The critical temperature and critical pressure of CO_2 are 31.0°C and 72.9 atm, respectively. Using the ideal gas equation, we obtain

$$P = \frac{nRT}{V} = \frac{0.5 \text{ mole} \times 0.0821 \text{ liter atm/deg mole} \times 300.15 \text{ deg}}{1 \text{ liter}}$$
$$= 12.32 \text{ atm}$$

Using the van der Waals equation, we obtain

$$a = \frac{27 \times (0.0821 \text{ liter atm/deg mole})^2 \times (304.15 \text{ deg})^2}{64 \times 72.9 \text{ atm}}$$
$$= 3.608 \text{ liter}^2 \text{ atm/mole}^2$$

$$b = \frac{(0.0821 \text{ liter atm/deg mole}) \times 304.15 \text{ deg}}{8 \times 72.9 \text{ atm}}$$
$$= 0.0428 \text{ liter/mole}$$

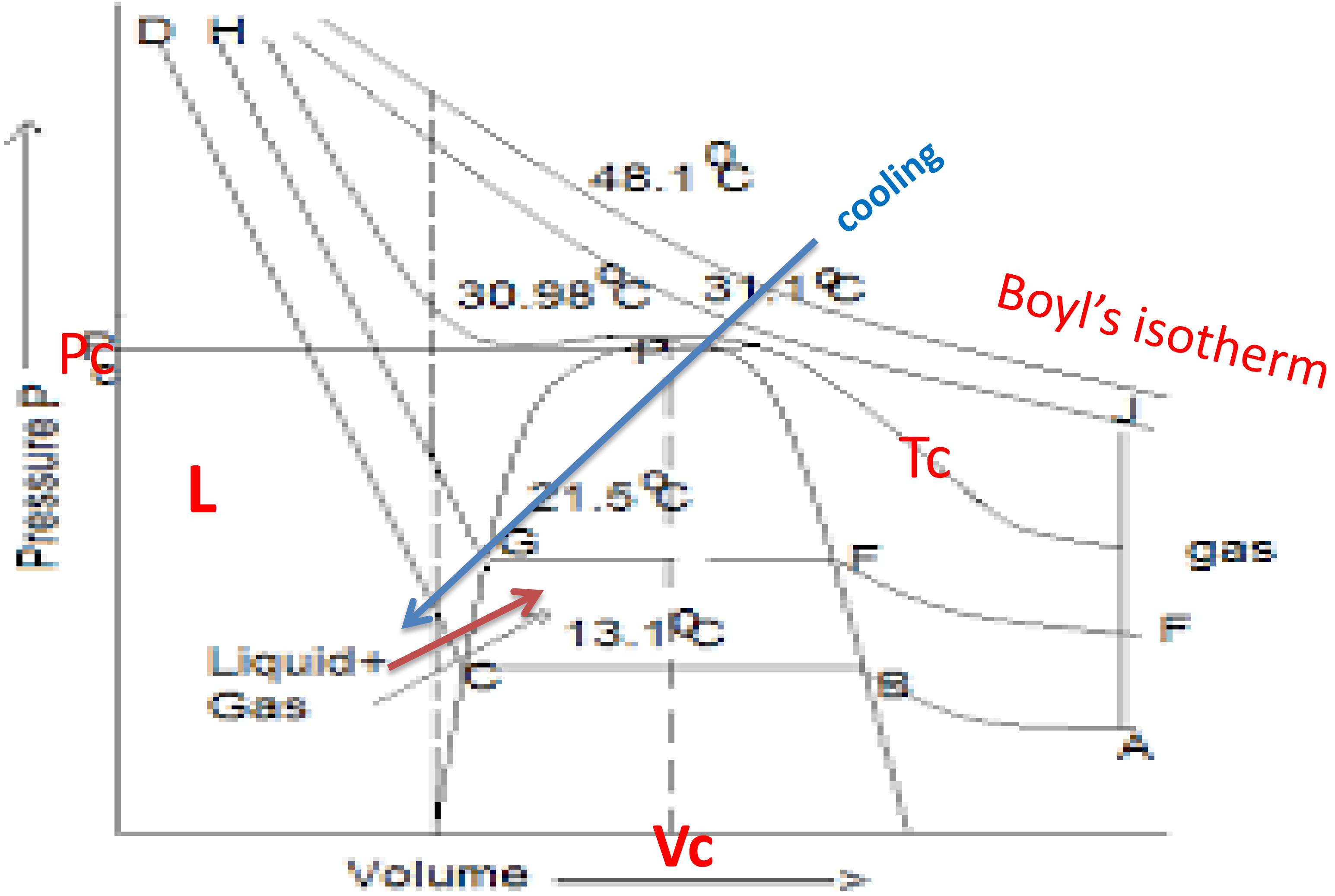
$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$
$$= \frac{(0.5 \text{ mole} \times 0.821 \text{ liter atm/deg mole}) \times 300.15 \text{ deg}}{1 \text{ liter} - (0.5 \text{ mole} \times 0.0428821 \text{ liter/mole})}$$
$$- \frac{(3.608 \text{ liter}^2 \text{ atm/mole}^2) \times 0.5 \text{ mole}^2}{(1 \text{ liter})^2}$$
$$= 11.69 \text{ atm}$$

Liquid state

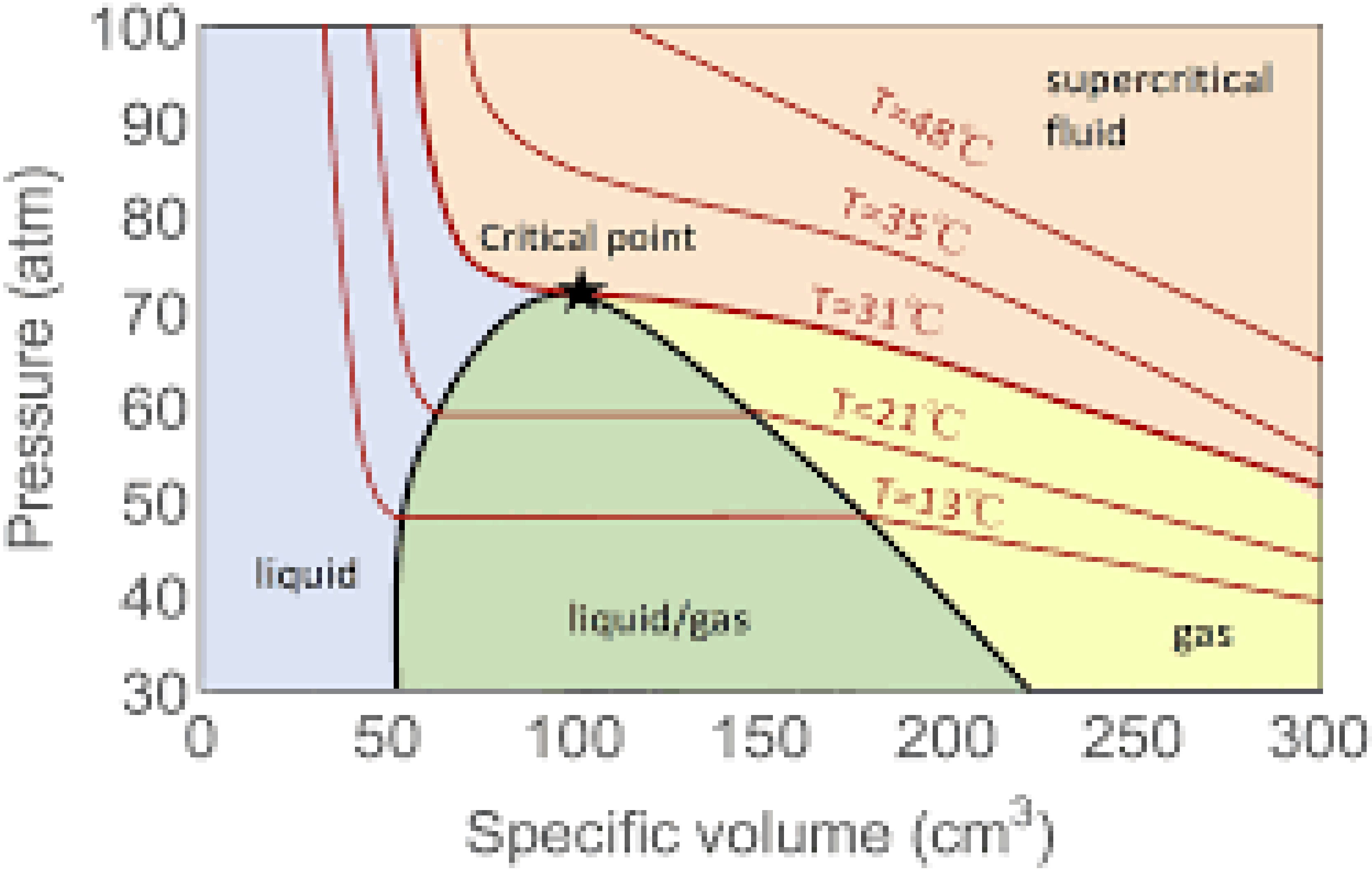
The liquid state has a moderate Intermolecular interaction and definite volume

Gases can be liquefied by cooling and pressing

Gas can be liquefied by increasing P below Tc, V will be shrinks



Andrews Isotherm of CO_2 gas


supercritical fluid
T=48°C
T=35°C
T=31°C
T=21°C
T=13°C
Critical point
liquid
liquid/gas
gas
Pressure (atm)
100
90
80
70
60
50
40
30
0
50
100
150
200
250
300
Specific volume (cm^3)

	Pc	Tc
H_2O;	218 atm.	617 ^{0}K
He;	2.26 atm	5.2 ^{0}K

Aerosol formation

- By liquefaction of gas phase using increasing P below Tc, reversible change stat of Gas-Liquid occur.
- Preparation of Pharmaceutical aerosol:

By a drug dissolving or suspending in (propellant), a material that is liquid under the pressure conditions inside the container, but that form gas under normal atmospheric condition.

Vapor pressure of liquids

- When a liquid placed in an evacuated container at constant T, liquid pass into gaseous phase (vapor). The P of saturated vapor is known (equilibrium vapor pressure). The relationship between v.p. and T ^{0}K of liquid expressed by:
- $\log(p_2/p^0) = \Delta H_v(T_2 - T_0)/2.303RTb_2Tb_0$
- Clausius-Clapyron equation
- ΔH_v: Heat of vaporization= 9720 cal.mol^{-1} for water
- P^0=1 atm. Tb_0= 100 0C =373.15 ^{0}K

Example 2-7

Application of the Clausius–Clapeyron Equation

Compute the vapor pressure of water at 120°C. The vapor pressure p_1 of water at 100°C is 1 atm, and ΔH_v may be taken as 9720 cal/mole for this temperature range. Thus,

$$\log \frac{p_2}{1.0} = \frac{9720 \times (393 - 373)}{2.303 \times 1.987 \times 393 \times 373}$$

$$p_2 = 1.95 \text{ atm}$$

The Clausius–Clapeyron equation can be written in a more general form,

$$\log p = -\frac{\Delta H_v}{2.303 R} \frac{1}{T} + \text{constant} \qquad (2\text{–}16)$$

or in natural logarithms,

$$\ln p = -\frac{\Delta H_v}{R} \frac{1}{T} + \text{constant} \qquad (2\text{–}17)$$

from which it is observed that a plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature results in a straight line, enabling one to compute the heat of vaporization of the liquid from the slope of the line.

Boiling point T_b

The temperature at which the vapor pressure of liquid equals to the external or atmospheric pressure. T_b depend on the attractive force between the molecules of liquid.

(B.P) or T_b:

H_2O>EtOH>CS_2>$(Et)_2O$>Butane>Isobutane>Propane>He

100, 78.3, 46.3, 34.6, -0.4, -10.2, -42.2, -269