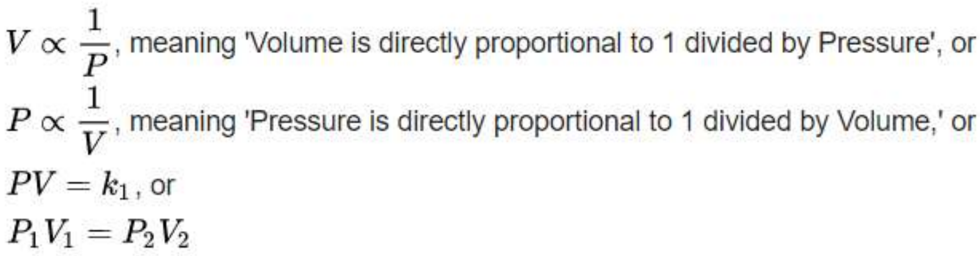
Chapter 2
Equations of State

2.1 Introduction

- The state of a homogeneous fluid can be described by an equation of the form:
$$f(P,V,T) = 0$$
- This equation is the resulted conclusion from experiments.
- This equation will have two independent variables.
- This equation does not contain time.
- Each system has its own equation of state.
- The equation of state doesn't involve time evolution since classical thermodynamics only deals with equilibrium states. That is, the system is in thermal, chemical, and mechanical equilibrium.

2.2 Equation of State of an Ideal Gas

- If we have a system composed of gas of mass m in kg whose molecular weight is M, its equation is approximately given by:
$$PV = \frac{m}{M}RT$$
Where R is a universal constant, having the same value for all gases:
$$R = 8.314 \times 10^3 \frac{J}{kilomole \cdot K}$$
- Since $n = {}^{m}/_{M}$ is the number of kilomoles of the gas, we can write:
$$PV = nRT$$
- This equation is called the equation of state of an ideal gas.
- The gas laws were developed at the end of the 18th century.
- Scientists began to realize that relationships between pressure, volume and temperature of a sample of gas could be obtained which would hold to approximation for all gases.
- Boyle's Law:



$V \propto \frac{1}{P}$, meaning 'Volume is directly proportional to 1 divided by Pressure', or

$P \propto \frac{1}{V}$, meaning 'Pressure is directly proportional to 1 divided by Volume,' or

$PV = k_1$, or

$P_1V_1 = P_2V_2$

Robert Boyle (1627-1691)

- Charles law:

$$V \propto T \text{, or}$$
$$V/T = k_2 \text{, or}$$
$$V_1/T_1 = V_2/T_2 \text{,}$$

Jacques Charles (1746-1823)

- Gay-Lussac's law:

$$P \propto T \text{, or}$$
$$P/T = k \text{, or}$$
$$P_1/T_1 = P_2/T_2 \text{,}$$

Joseph Gay-Lussac (1778-1850)

- Avogadro’s Law (1811):

$$\frac{V_1}{n_1} = \frac{V_2}{n_2}$$

Amedeo Avogadro (1776-1856)

- The ideal gas equation is obtained by combining Boyle's Law, Charles' Law, Gay-Lussac's Law:

$$V \propto \frac{T}{P}$$

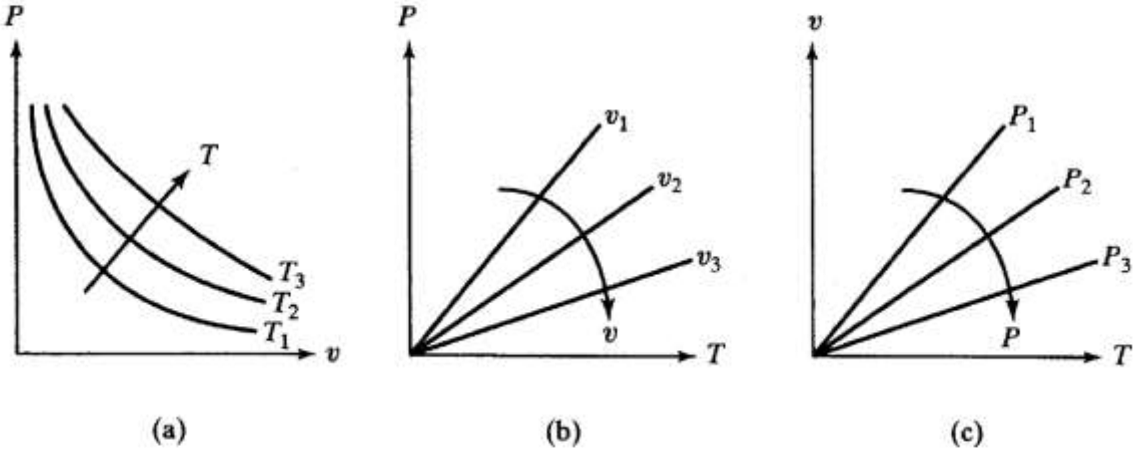
$$\frac{PV}{T} = C$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

- If we define the specific volume $v = V/n$, the ideal gas law becomes:

$$Pv = RT$$

- The projections of the surface $f(P, v, T) = 0$ on the P-v plane, the P-T plane, and the v-T plane are shown in the figure.



(a) (b) (c)

Figure 2.1 Diagrams for an ideal gas. In (a) the isotherms are equilateral hyperbolae; in (b) the isochores are straight lines; and in (c) the isobars are also straight lines.

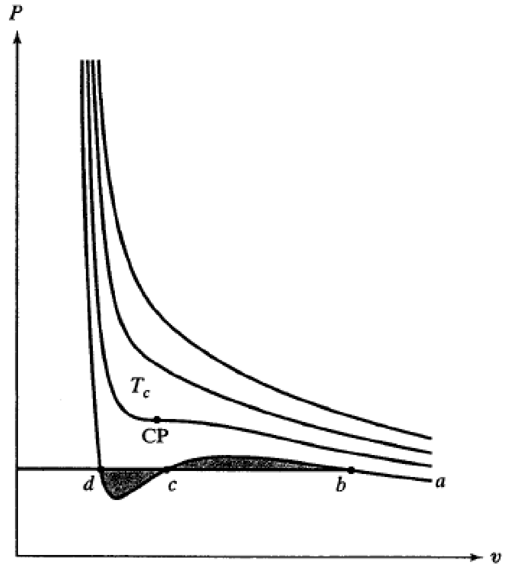
2.3 Van Der Waals Equation for a Real Gas

- The ideal gas law works well for high temperatures and low pressures.
- However, when the temperature and pressure are near condensation, deviations from the ideal gas law are observed.
- Van Der Waals equation represent a good model for real gases because of its simplicity and because it describes the behavior of many substances over a wide range of temperatures and pressures.
- His equation is:

$$\left(P+\frac{a}{v^2}\right)(v-b)=RT$$

Where a and b are characteristic constants for a given substance that depend only on the critical properties of the given material.

- The term a/v^2 arises from the intermolecular forces due to the overlap of electrons clouds.
- The constant b takes into account the finite volume occupied by the molecules; its effect is to be subtracted from the volume occupied.
- Van Der Waals equation reduces to the ideal gas equation for the case when $a = b = 0$.
- The Figure below shows some isotherms calculated from the Van der Waals equation.



- As T increases, the curves approach $Pv = constant$. The correction factors become less important.
- For $T < T_c$ there is a local maximum and local minimum for P.
- The region for which $T < T_c$ is considered unstable since the pressure no longer increases as the volume is diminished.
- Actually, the gas never traverses the portion of the curve between b and d because the gas undergoes a change of phase.
- If the compression process starts at a, part of the gas will begin to liquify at b and the pressure remains constant as the volume is further decreased as long as the temperature is held constant.
- Between b and d, liquid and vapor are in equilibrium.
- Finally, at d, liquification is complete.
- After that, the pressure rises sharply as the volume is decreased which is characteristic of a liquid.
- For $T \geq T_c$, the curve has no minima or maxima. Above T_c, it is impossible to liquify a gas, no matter how large the pressure is.
- The critical values v_c, T_c, and P_c of a substance can be expressed in terms of the constants a and b that appear in the Van der Waals equation for $T = T_c$:

$$P_c = \frac{RT_c}{v_c - b} - \frac{a}{v_c^2} \quad \& \quad \left(\frac{\partial P}{\partial v}\right)_c = 0 \quad \& \quad \left(\frac{\partial^2 P}{\partial v^2}\right)_c = 0$$

$$\rightarrow v_c = 3b$$

$$\rightarrow T_c = \frac{8a}{27Rb}$$

$$\rightarrow P_c = \frac{a}{27b^2}$$

- Alternatively, we may solve for the constants a and b in terms of the critical values as follows:

$$a = \frac{27R^2T_{\mathrm{cr}}^2}{64P_{\mathrm{cr}}} \quad \text{and} \quad b = \frac{RT_{\mathrm{cr}}}{8P_{\mathrm{cr}}}$$

And get the critical properties from a thermophysical properties table.

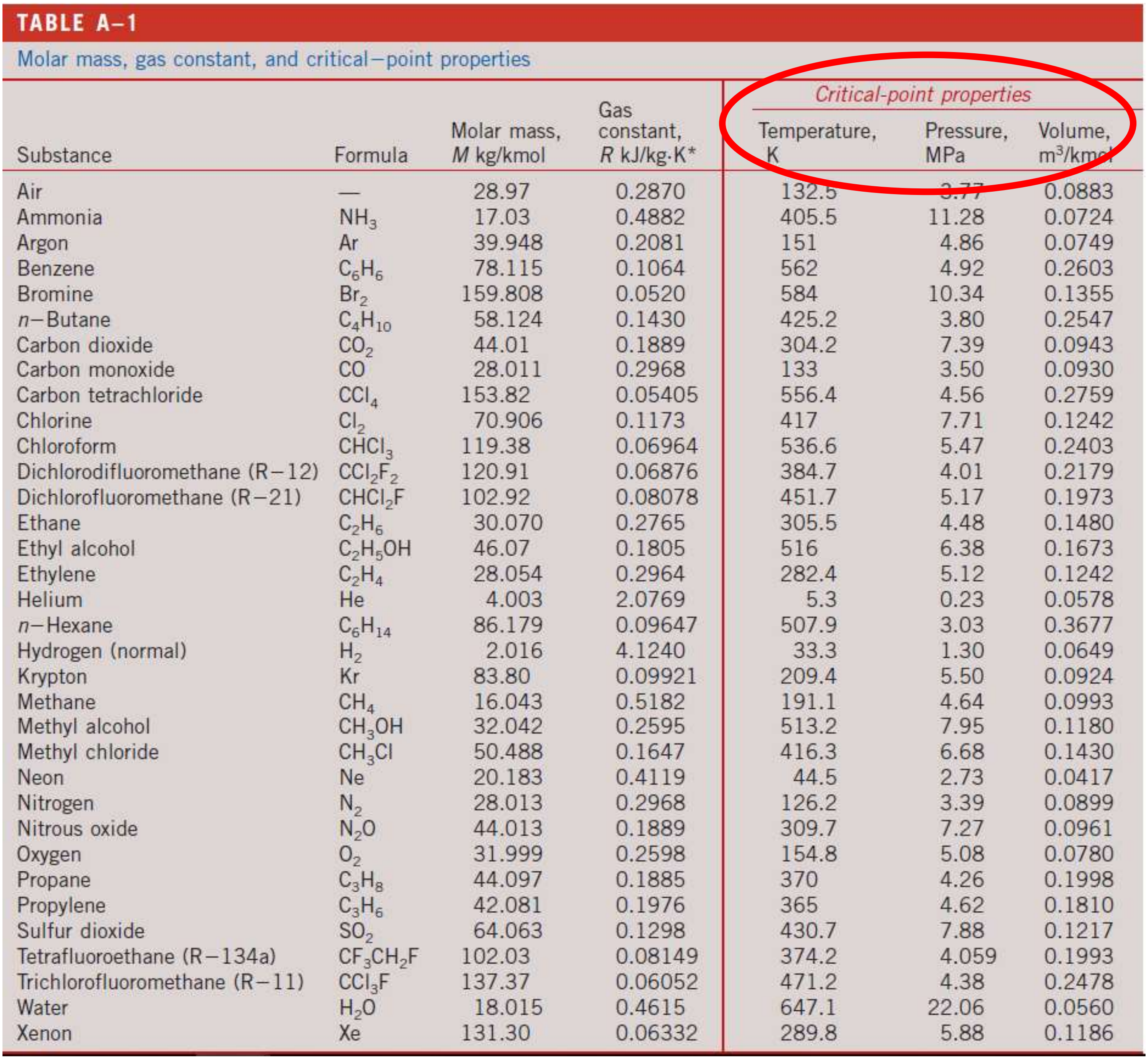


TABLE A–1

Molar mass, gas constant, and critical–point properties

Substance	Formula	Molar mass, *M* kg/kmol	Gas constant, *R* kJ/kg·K*	*Critical-point properties*		
				Temperature, K	Pressure, MPa	Volume, m^3/kmol
Air	—	28.97	0.2870	132.5	3.77	0.0883
Ammonia	NH_3	17.03	0.4882	405.5	11.28	0.0724
Argon	Ar	39.948	0.2081	151	4.86	0.0749
Benzene	C_6H_6	78.115	0.1064	562	4.92	0.2603
Bromine	Br_2	159.808	0.0520	584	10.34	0.1355
n–Butane	C_4H_{10}	58.124	0.1430	425.2	3.80	0.2547
Carbon dioxide	CO_2	44.01	0.1889	304.2	7.39	0.0943
Carbon monoxide	CO	28.011	0.2968	133	3.50	0.0930
Carbon tetrachloride	CCl_4	153.82	0.05405	556.4	4.56	0.2759
Chlorine	Cl_2	70.906	0.1173	417	7.71	0.1242
Chloroform	$CHCl_3$	119.38	0.06964	536.6	5.47	0.2403
Dichlorodifluoromethane (R–12)	CCl_2F_2	120.91	0.06876	384.7	4.01	0.2179
Dichlorofluoromethane (R–21)	$CHCl_2F$	102.92	0.08078	451.7	5.17	0.1973
Ethane	C_2H_6	30.070	0.2765	305.5	4.48	0.1480
Ethyl alcohol	C_2H_5OH	46.07	0.1805	516	6.38	0.1673
Ethylene	C_2H_4	28.054	0.2964	282.4	5.12	0.1242
Helium	He	4.003	2.0769	5.3	0.23	0.0578
n–Hexane	C_6H_{14}	86.179	0.09647	507.9	3.03	0.3677
Hydrogen (normal)	H_2	2.016	4.1240	33.3	1.30	0.0649
Krypton	Kr	83.80	0.09921	209.4	5.50	0.0924
Methane	CH_4	16.043	0.5182	191.1	4.64	0.0993
Methyl alcohol	CH_3OH	32.042	0.2595	513.2	7.95	0.1180
Methyl chloride	CH_3Cl	50.488	0.1647	416.3	6.68	0.1430
Neon	Ne	20.183	0.4119	44.5	2.73	0.0417
Nitrogen	N_2	28.013	0.2968	126.2	3.39	0.0899
Nitrous oxide	N_2O	44.013	0.1889	309.7	7.27	0.0961
Oxygen	O_2	31.999	0.2598	154.8	5.08	0.0780
Propane	C_3H_8	44.097	0.1885	370	4.26	0.1998
Propylene	C_3H_6	42.081	0.1976	365	4.62	0.1810
Sulfur dioxide	SO_2	64.063	0.1298	430.7	7.88	0.1217
Tetrafluoroethane (R–134a)	CF_3CH_2F	102.03	0.08149	374.2	4.059	0.1993
Trichlorofluoromethane (R–11)	CCl_3F	137.37	0.06052	471.2	4.38	0.2478
Water	H_2O	18.015	0.4615	647.1	22.06	0.0560
Xenon	Xe	131.30	0.06332	289.8	5.88	0.1186

2.4 P-v-T Surfaces for Real Substances

- The P-v-T surface for a pure substance is shown in the Figure below.

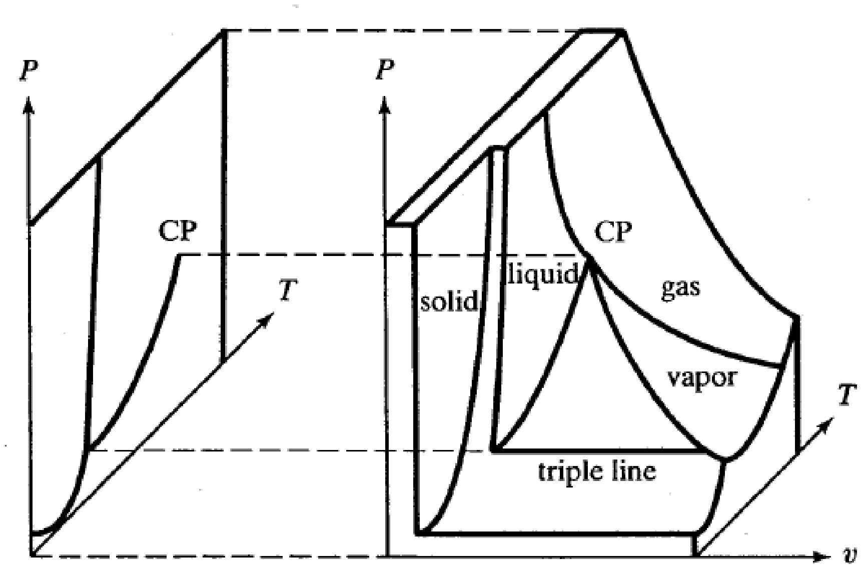


Figure 2.3 *P-v-T* surface for a substance that contracts on freezing.

- On the left is the projection of the P-v-T surface on a P-T diagram.
- TP stands for the triple line where all the three phases can coexist.
- CP stands for the critical point where there is no discernable interface between the two phases.
- The projection of the surfaces on the P-T plane is of special interest and is shown below.

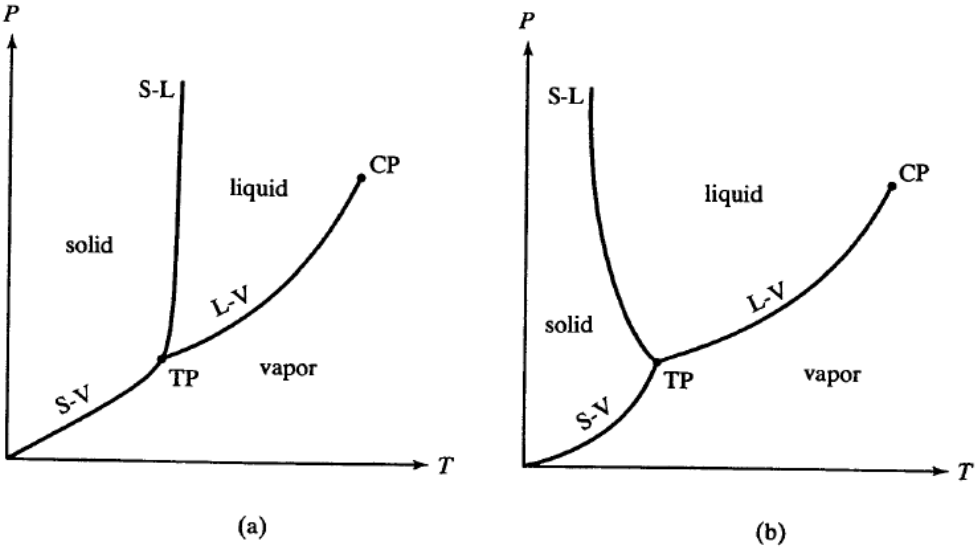


Figure 2.4 *P-T* diagrams for (a) a substance that contracts on freezing; and (b) a substance that expands on freezing.

- The L-V curve is the vapor pressure curve, for which the liquid and vapor can coexist in equilibrium. It is known as the saturated vapor curve.
- The S-L curve is the freezing point curve.
- The S-V curve is the sublimation curve.
- No critical point can exist for solid-liquid equilibrium (S-L curve). This is because solids and liquids possess different symmetry properties. A normal liquid is isotropic, whereas a

solid has a crystalline structure whose orientation defines a particular set of directions. The transition from one symmetry to another is strictly a discontinues process.

2.5 Expansivity and Compressibility

- Suppose we want to develop an equation of state for a solid or liquid.
- Then, writing the equation of state is written in this form:

$$v = v(T, P).$$

- Taking the differential:

$$dv = \left(\frac{\partial v}{\partial T}\right)_P dT + \left(\frac{\partial v}{\partial P}\right)_T dP.$$

- Defining the coefficient of expansivity:

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \quad \Rightarrow \quad \Delta v = \left(\frac{\partial v}{\partial T}\right)_P \Delta T = v\beta\Delta T$$

- Defining the isothermal compressibility as:

$$\kappa = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \quad \Rightarrow \quad \Delta v = \left(\frac{\partial v}{\partial P}\right)_T \Delta P = -v\kappa\Delta P$$

- For an ideal gas, $v = RT/P$ and:

$$\beta = \frac{1}{v}\left(\frac{R}{P}\right) = \frac{1}{T}.$$

$$\kappa = -\frac{1}{v}\left(-\frac{RT}{P^2}\right) = \frac{1}{P}.$$

- For liquids and solids, β and κ are nearly constant across a wide range of temperature and pressures.
- Also, we can take $v \approx v_o$.
- Substituting, β and κ back to dv gives:

$$dv = \beta v dT - \kappa v dP.$$

$$dv \approx \beta v_0 dT - \kappa v_0 dP.$$

- And integrating:

$$\int_{v_0}^{v} dv = \beta v_0 \int_{T_0}^{T} dT - \kappa v_0 \int_{P_0}^{P} dP,$$

- We get:

$$v = v_0[1 + \beta(T - T_0) - \kappa(P - P_0)].$$

- This is an approximation equation of a state for a liquid or a solid. The volume increases linearly with an increase in temperature and decreases linearly with an increase in pressure.

2.6 An Application

- Suppose we want to calculate the decrease in pressure of a fluid when it is cooled from T_1 to T_2.

- We know that the equilibrium states of the fluid are fixed by specifying two state variables that are related by some equation of state:

$$f(P, v, T) = 0 \rightarrow P = P(v, T)$$

- We assume that the process in which the fluid is changed from an equilibrium state (P_1, T_1) to another equilibrium state (P_2, T_2) is isochoric—that is, the volume is unchanged.
- We assume that the fluid is cooled reversibly.
- Taking the differential:

$$dP = \left(\frac{\partial P}{\partial v}\right)_T dv + \left(\frac{\partial P}{\partial T}\right)_v dT.$$

- Since the process is isochoric, $dv = 0$:

$$P_2 - P_1 = \int_{T_1}^{T_2} \left(\frac{\partial P}{\partial T}\right)_v dT.$$

- Unfortunately, the integrand is unknown. However, using the cyclical relation given in Appendix A, we have:

$$\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_P \left(\frac{\partial v}{\partial P}\right)_T = -1.$$

- Thus,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P} = \frac{-\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\beta}{\kappa}$$

- Substituting this result back in the integral, we have:

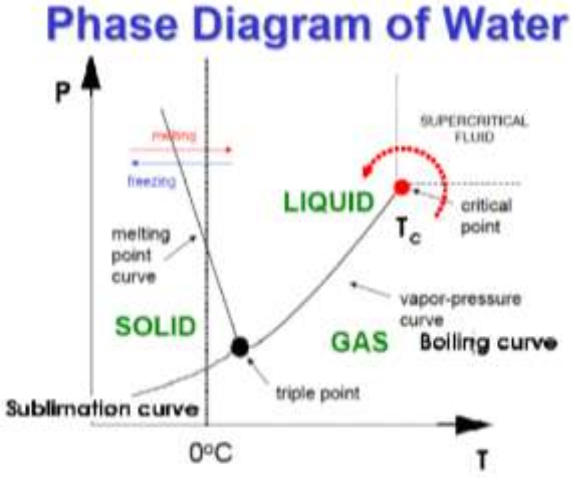
$$P_2 - P_1 = \frac{\beta}{\kappa}(T_2 - T_1),$$

- Be careful! Cooling in reality would introduce large temperature gradients in the bulk of the material and the environment surrounding it.
- Consequently, the intermediate states are not equilibrium ones.

QUESTION: Equations of state are formulated for equilibrium states. However, we have shown that the intermediate states are not equilibrium ones. Can this equation still be considered an equation of state? or not?

Answer: $P, v, and\ T$ are all exact differentials whose integrals are independent of path. Thus, even though the process goes through nonequilibrium intermediate states, the final states are equilibrium states, and it doesn't matter which path we took to get from state 1 to state 2. We chose a reversible path because of its convenience.
ΔP is independent of the path.

Appendix 1



Phase: A portion of the system under consideration that is sub-macroscopically homogeneous and is separated from other such portions by definite physical boundary.

Coexistence lines: The boundary lines between phases.

Phase Transition (**PT**): Transition between two equilibrium phases of matter whose signature is a singularity or discontinuity in some observable quantity.

Critical point (**CP**): a point on a phase diagram at which both the liquid and gas phases of a substance have the same density, and are therefore indistinguishable.

Appendix 2

Thermal Expansion

For the expression:

$$V_f = V_i\left[1+\beta(T_f - T_i) - \kappa(P_f - P_i)\right]$$

We can define the following:

☞ **Expansively** or Coefficient of Volume Expansion, $\beta(T,P)$.

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \quad \Rightarrow \quad \Delta V = \left(\frac{\partial V}{\partial T}\right)_P \Delta T = V\beta\Delta T$$

Usually, β is positive. An exception is water in the temperature range between 0° C and 4° C.

Range of β is about:

β » 10^{-3} for gasses.

β » 10^{-5} for solids.

☞ **Compressibility:** Volume also depends on pressure. Isothermal Compressibility $\kappa(T,P)$:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \Rightarrow \quad \Delta V = \left(\frac{\partial V}{\partial P}\right)_T \Delta P = -V\kappa\Delta P$$

$$\text{Bulk Modulus} = \frac{1}{\kappa} = -V\left(\frac{\partial P}{\partial V}\right)_T$$

A Little Calculus

$$\text{Consider, } V(T,P) \quad \Rightarrow \quad dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\text{If, } V = \text{const},\ dV = 0$$

$$\left(\frac{\partial V}{\partial T}\right)_P dT_V + \left(\frac{\partial V}{\partial P}\right)_T dP_V = 0$$

Cyclical Relation

$$\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V = 0$$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P = -1$$

Application

Suppose you need: $\left(\frac{\partial P}{\partial T}\right)_V$

$$\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P = -1$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{-1}{\left(\frac{\partial V}{\partial P}\right)_T \left(\frac{\partial T}{\partial V}\right)_P} = \frac{-\left(\frac{\partial V}{\partial T}\right)_P}{\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T} = \frac{\beta}{\kappa}$$