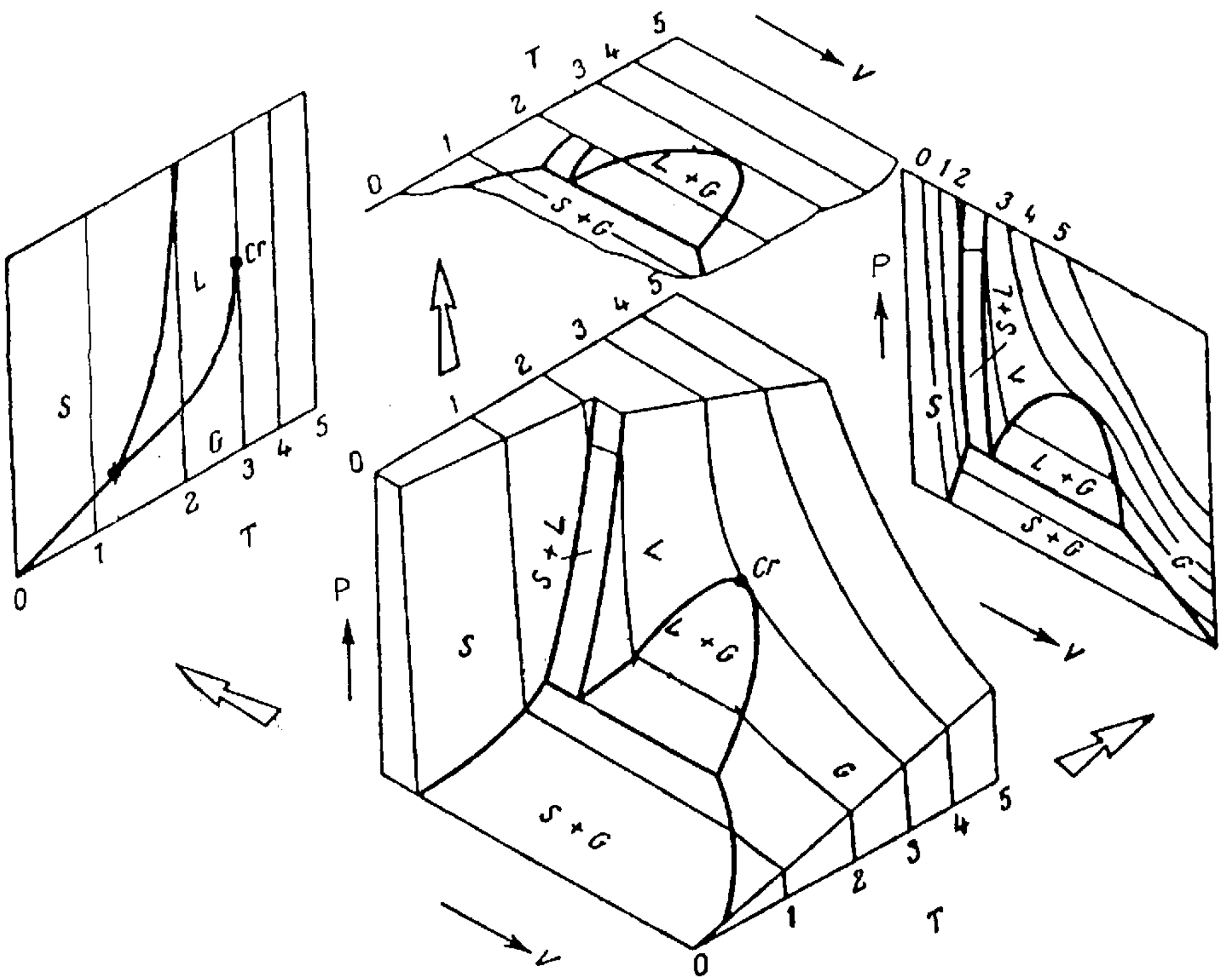
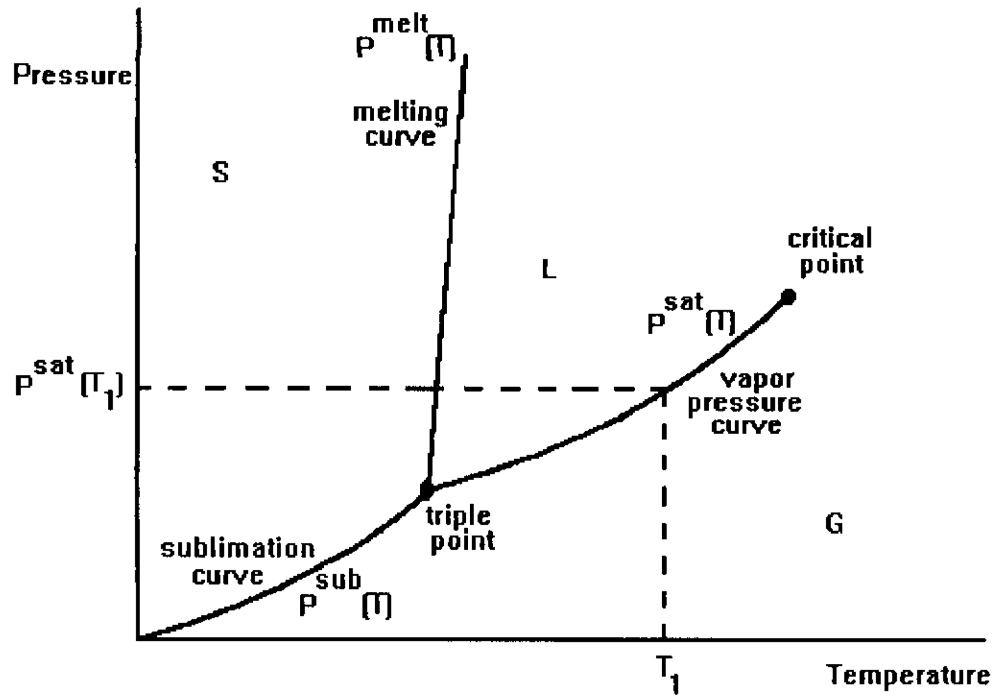
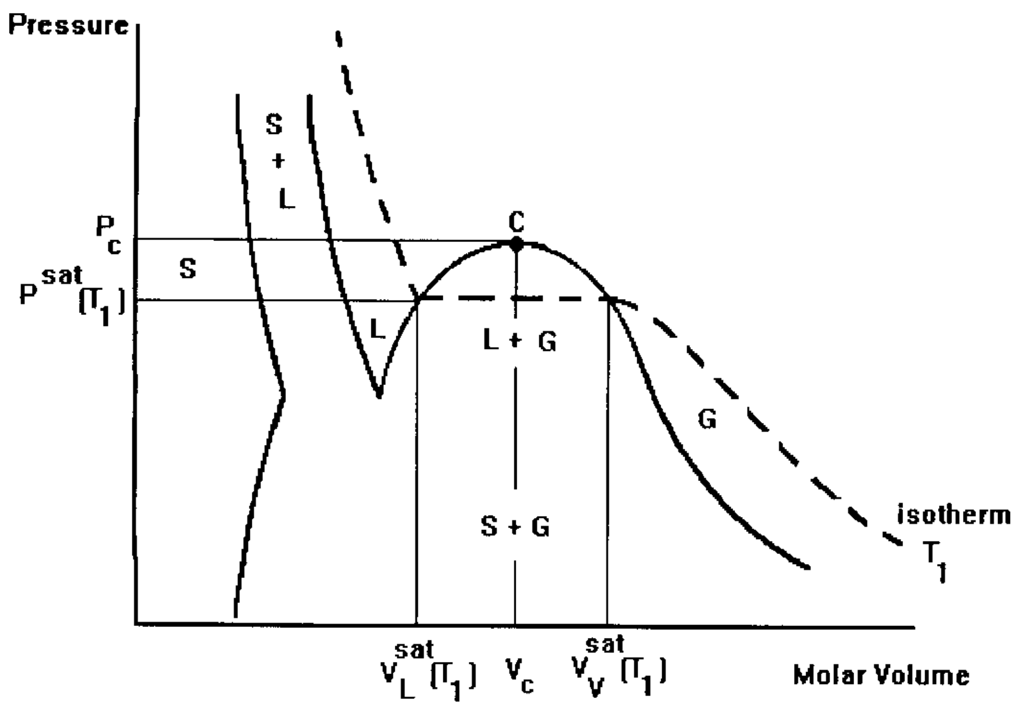
Phase Diagram of a Pure Substance

Three-Dimensional Surface and Two-Dimensional Projections



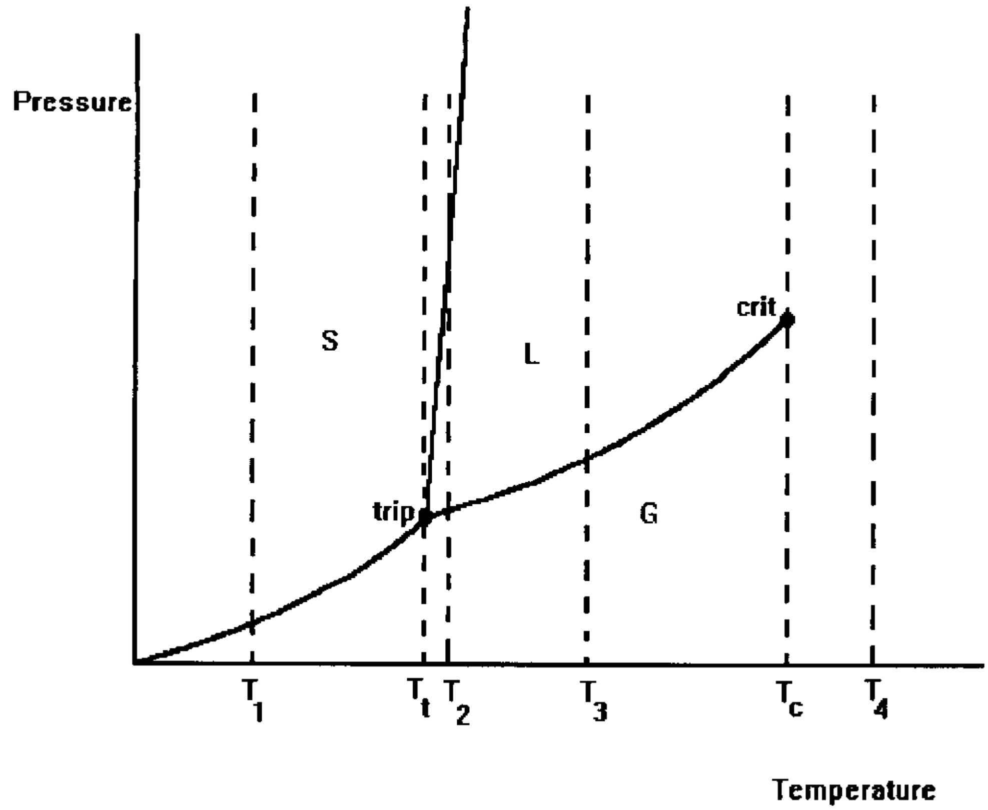
Handout #1

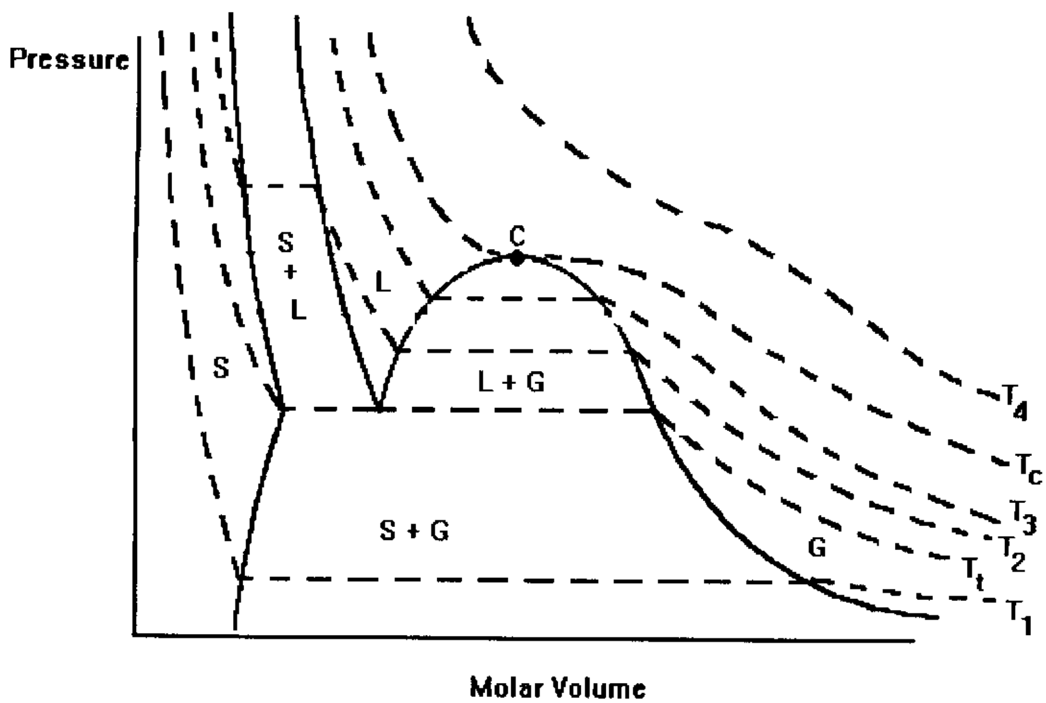




Pressure-Temperature and Pressure-Volume Projections for a Typical Pure Substance

Handout # 1A

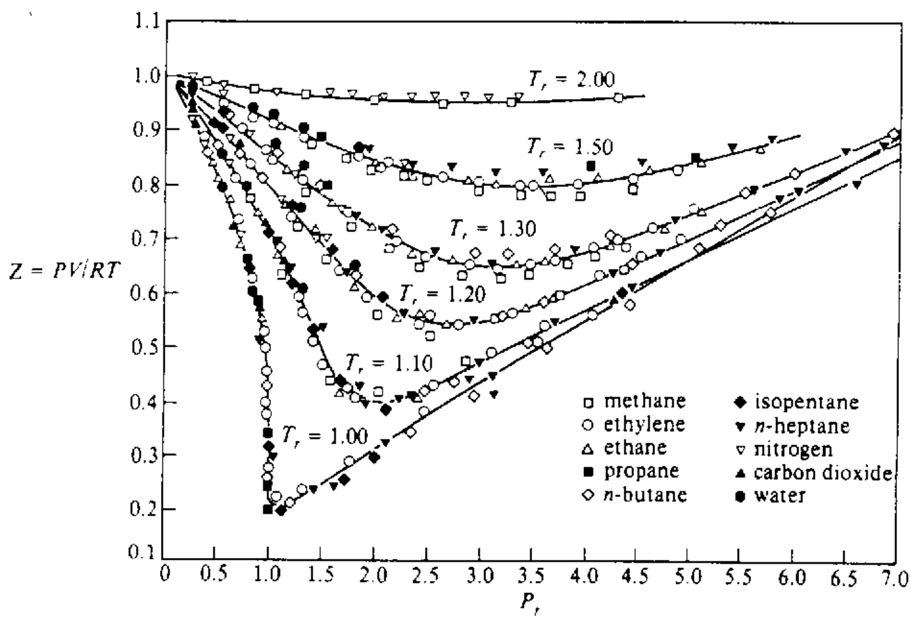




Pressure-Temperature and Pressure-Volume Projections
Showing Several Different Isotherms

Handout # 1B

Illustration of the Principle of Corresponding States



Two-parameter corresponding-states correlation of the compressibility factor Z

Handout #2

Table of Thermodynamic Functions for Constant Composition Fluids

Function	Definition	Property Relation	Natural Independent Variables	Total Differential	Maxwell Relation
U		$dU = TdS - PdV$	S, V	$dU = (\partial U/\partial S)_V\, dS + (\partial U/\partial V)_S\, dV$	$(\partial P/\partial S)_V = -(\partial T/\partial V)_S$
H	$H = U + PV$	$dH = TdS + VdP$	S, P	$dH = (\partial H/\partial S)_P\, dS + (\partial H/\partial P)_S\, dP$	$(\partial V/\partial S)_P = (\partial T/\partial P)_S$
A	$A = U - TS$	$dA = -SdT - PdV$	T, V	$dA = (\partial A/\partial T)_V\, dT + (\partial A/\partial V)_T\, dV$	$(\partial P/\partial T)_V = (\partial S/\partial V)_T$
G	$G = H - TS$	$dG = -SdT + VdP$	T, P	$dG = (\partial G/\partial T)_P\, dT + (\partial G/\partial P)_T\, dP$	$(\partial V/\partial T)_P = -(\partial S/\partial P)_T$

Handout #3

Formulas for Residual Properties and Fugacity Coefficient

For equations of state solved easily for *volume:*

$$S^R = \int_0^P \left[\frac{R}{P} - \left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

$$H^R = \int_0^P \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP$$

$$\ln \varphi = \int_0^P \frac{(Z - 1)}{P}\, dP$$

For equations of state solved easily for *pressure:*

$$S^R = R \ln Z - \int_\infty^V \left[\frac{R}{V} - \left(\frac{\partial P}{\partial T}\right)_V\right] dV$$

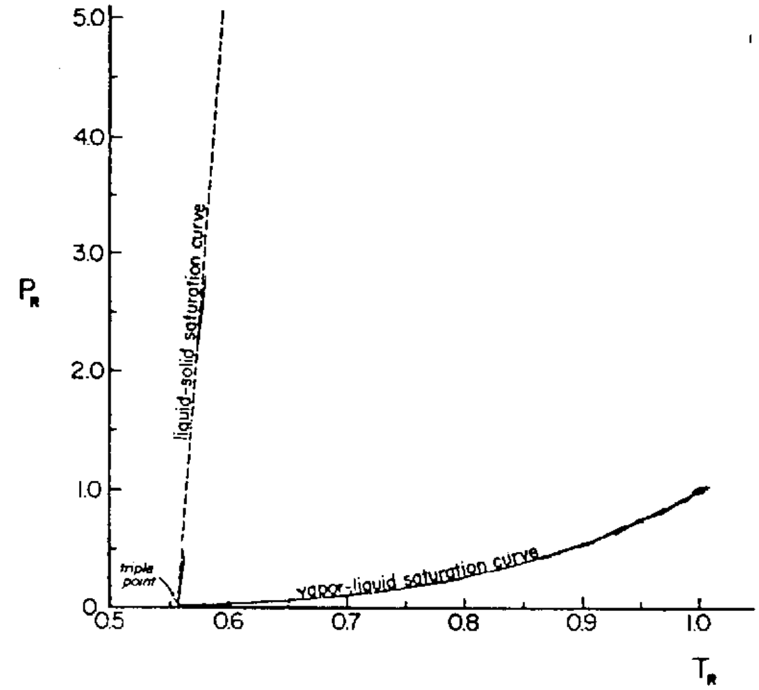
$$H^R = RT(Z - 1) - \int_\infty^V \left[P - T\left(\frac{\partial P}{\partial T}\right)_V\right] dV$$

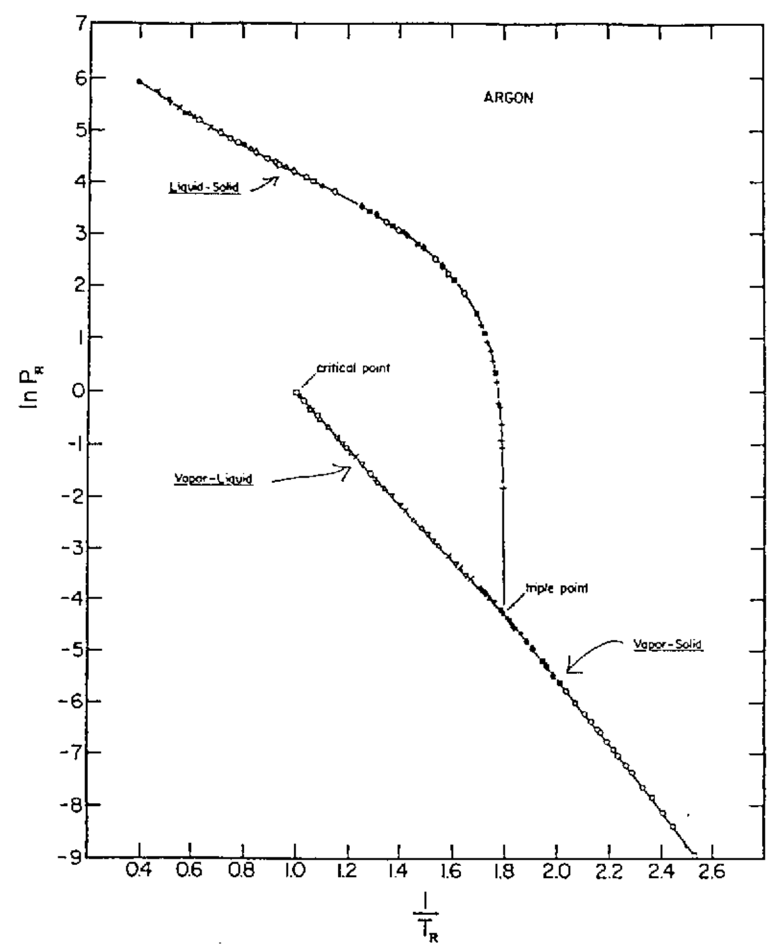
$$\ln \varphi = \frac{1}{RT}\int_\infty^V \left(\frac{RT}{V} - P\right) dV - \ln Z + Z - 1$$

Handout #4

Two Phase Behavior of Argon on P-T and ln P - 1/T coordinates

Note that the liquid-vapor and solid-vapor lines on the bottom graph are nearly straight.





Handout #5

Some Early and Recent Vapor Pressure Equations

	1. $\ln P = (k_1 + k_2 T) \ln T$	Schmidt (1797)
	2. $\ln P = k_1 \ln (k_2 + k_3 T)$	Young (1807)
	3. $\ln P = k_1 T/(T + k_2)$	Wrede (1841)
	4. $\ln P = k_1 - k_2/T - k_3 T^2$	Rankine (1849); Kirchhoff (1858)
*	5. $\ln P = k_1 - k_2/(T + k_3)$	Antoine (1888)
	6. $\ln (P_c/P) = k(T_c/T - 1), k \simeq 3$	van der Waals (1899)
	7. $P_r(V_g - V_L) = RT(1 - P_r)$	Nernst (1906)
	8. $\ln P_r = (1 - 1/T_r)(k_1 - k_2 \ln T_r)$	Carbonelli (1919)
	9. $\ln P = k_1 + k_2/T + k_3 T + k_4 T^2$	Cragoe (1928) (Int. Crit, Tables III, p. 228)
	10. $\ln P = k(T_c/T - 1) + (T_c/T) \ln P_c$	Pollara (1942)
	11. $\ln P = k_1 + k_2/T + k_3 \ln T + k_4 P/T^2$	Frost & Kalkwarf (1953) Harlacher & Braun (1970); Reid, Prausnitz, & Sherwood (1977, p. 188)
	12. $\ln P = k_1 + k_2/T + k_3 T + k_4 T^3$	Miller (1964)
**	13. $T_r \ln P_r = k_1 \tau + k_2 \tau^{1.5} + k_3 \tau^3 + k_4 \tau^6$ $\tau = 1 - T/T_c$	Wagner (1973); Ambrose (1978)

* Popular for applications at low pressure (below 1 to 2 bars)

** Currently popular for use over the entire range between the triple point and critical point

Handout #6

Analytical Solution for Cubic Equations of State

Consider van der Waals equation:

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \qquad \textit{where} \qquad a = \frac{27R^2T_c^2}{64P_c} \qquad b = \frac{RT_c}{8P_c}$$

By multiplying through by $P^2V^2(V-b)/R^3T^3$ the equation may also be expressed as

$$Z^3 - Z^2(1 + \beta) + \alpha Z - \alpha\beta = 0 \qquad (1)$$

where

$$Z = \frac{PV}{RT}$$

$$\alpha = \frac{aP}{R^2T^2} = \frac{27PT_c^2}{64P_cT^2}$$

$$\beta = \frac{bP}{RT} = \frac{PT_c}{8P_cT}$$

In saturation calculations, it is necessary to solve equation (1) (at a given temperature and an assumed pressure) for two roots $Z_{sat\ liq}$ and $Z_{sat\ vap}$. Although this may be done numerically, you may wish to take advantage of the analytical solution for a general cubic equation which is summarized below.

Analytical Solution to Cubic Equation

Goal: Solve $Z^3 + (E_1)Z^2 + (E_2)Z + (E_3) = 0$ for all Z roots.

Method : Calculate the following quantities

$$Q = \frac{3E_2 - E_1^2}{9} \qquad R = \frac{9E_1E_2 - 27E_3 - 2E_1^3}{54} \qquad D = Q^3 + R^2$$

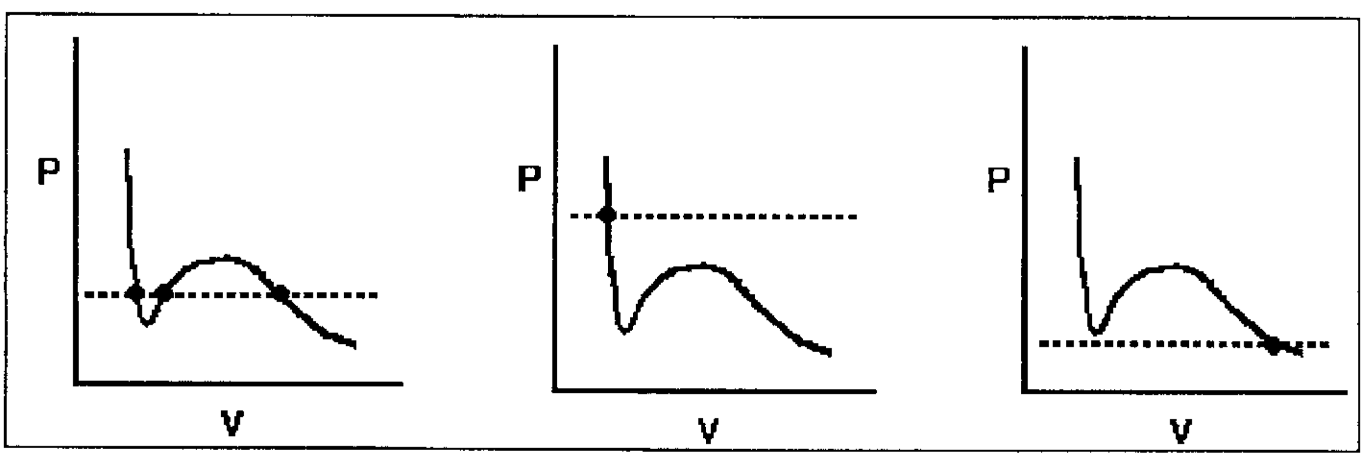
If D<0 then there are 3 real roots to the equation. These are given by

$$Z_i = 2\sqrt{-Q}\cos\left(\frac{\theta}{3} + 120i\right) - \frac{E_1}{3}$$

where i = 0, 1 and 2. The angle **θ** is in degrees and is obtained from:

$$\theta = \cos^{-1}\left(\frac{R}{\sqrt{-Q^3}}\right) = \tan^{-1}\left(\frac{\sqrt{-D}}{R}\right)$$

If D>0 there is 1 real root and 2 complex roots. These may be obtained from a different method. Note however that in saturation calculations we *want* 3 real roots. If you get only 1 real root (i.e. D<0) then you have made a bad guess for P^{sat}. This concept is illustrated below.



Reasonable first guess for P^{sat} (D<0)

bad first guesses for P^{sat} (D>0)