

# ChBE BIBLE

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# Contents

<b>1</b>	<b>Thermodynamics</b>	<b>2</b>
1.1	Equations of State . . . . .	2
1.1.1	Ideal Gas Law . . . . .	3
1.1.2	Cubic EOS . . . . .	3
1.1.3	Virial Equation . . . . .	3
1.2	Saturation Properties . . . . .	4
1.2.1	Molar Volume - Saturated Liquid . . . . .	4
1.2.2	Saturated Vapor Pressure . . . . .	5
<b>2</b>	<b>Transport Phenomena</b>	<b>8</b>

# Chapter 1

## Thermodynamics

### 1.1 Equations of State

An equation of state (EOS) is a mathematical model that describes the PVT behavior of a compound. This section explores several models that described the vapor, liquid and supercritical phases and the associated Matlab programs. These models can be utilized for several purposes like calculating PVT, the compressibility, the fugacity coefficient, or residual properties.

The Gibbs phase rule states

$$^{\circ}F = 2 - \pi + N \quad (1.1)$$

where  $^{\circ}F$  is degrees of freedom,  $\pi$  is the number of phases, and  $N$  is the number of species. This implies that by setting two extensive variables for a single phase, other extensive variables may be calculated by the EOS. Since only pressure, temperature, and volume may be directly measured in a laboratory setting, the EOS is expressed in terms of these extensive variables. However, additional extensive variables may be calculated by slightly modifying the EOS. In particular, the extensive variables of compressibility, fugacity coefficient and residual properties are incredibly important in common chemical engineering problems.

The compressibility is defined as

$$Z = \frac{\bar{V}}{\bar{V}^{ig}} = \frac{\bar{V}P}{RT} \quad (1.2)$$

The fugacity coefficient is

$$\ln(\phi) = \int_0^P (Z - 1) \frac{dP}{P} \quad (1.3)$$

A residual is defined as the difference between a property in the real state versus the ideal gas state.

$$M^R = M - M^{ig} \quad (1.4)$$

Since, enthalpy, Gibbs free energy, and entropy are state variables the relationship between these variables and pressure can be expressed in the residual properties. Thus the residuals are (without showing the derivation): Enthalpy

$$\frac{H^R}{RT} = -T \int_0^P (Z - 1) \frac{dP}{P} (@const.T) \quad (1.5)$$

Gibbs Free Energy

$$\frac{G^R}{RT} = \int_0^P (Z - 1) \frac{dP}{P} \quad (@const.T) \quad (1.6)$$

Entropy

$$\frac{S^R}{R} = -T \int_0^P \left( \frac{\partial Z}{\partial T} \right)_P \frac{dP}{P} - \int_0^P (Z - 1)_P \frac{dP}{P} \quad (@const.T) \quad (1.7)$$

### 1.1.1 Ideal Gas Law

The ideal gas law is

$$P\bar{V} = RT \quad (1.8)$$

The program IdealGas.m, like all the following EoS programmed into Matlab calculate PVT, Z, & the Fugacity Coefficient. As a heuristic rule, never use the Ideal Gas law above 10 bars.

### 1.1.2 Cubic EOS

Several forms of a cubic EOS have been proposed. The first was proposed by van der Waal (1890). All cubic EOS have the general form

$$P = \frac{RT}{\bar{V} - b} - \frac{a}{(V + \epsilon b)(V + \sigma b)} \quad (1.9)$$

For the various models, different values of b,  $\epsilon$ , and  $\sigma$  are used for each EoS. The parameter a is described as a function of temperature and acentric factor to obtain the proper curvature for the EoS. As a general heuristic rule van der Waals is the least accurate cubic EoS which Soave-Redlich-Kwong and Peng-Robinson are among the better ones available. They were designed to be accurate below the critical properties and should not be extended very far above  $T_r = 2$  or at high pressures.

Four models are currently available in Matlab: van der Waals (VanDerWaals.m), Redlich-Kwong (RedlichKwong.m), Soave-Redlich-Kwong (SRK.m), & Peng-Robinson (PengRobinson.m).

### 1.1.3 Virial Equation

Volume Expansion

$$Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \dots \quad (1.10)$$

Pressure Expansion

$$Z = 1 + \frac{BP}{RT} + (C - B^2) \left( \frac{P}{RT} \right)^2 + \dots \quad (1.11)$$

For normal, simple compounds (i.e. alkanes, diatomics, etc.) Lee-Kelser approximation of B can be utilized in Pitzer2ndVirial.m. This is accurate to  $T_r < 1.5$  and moderate pressure ranges.

## 1.2 Saturation Properties

### 1.2.1 Molar Volume - Saturated Liquid

Numerous techniques are available to estimate the molar volume of a saturated liquid. The following algorithms were programmed into Vsat.m

Rackett (1970)

$$V_{sat} = V_c Z_c^{(1-T_r)^{\frac{2}{7}}} \quad (1.12)$$

Modified Rackett (1970)

$$V_{sat} = \frac{RT_c}{P_c} Z_c^{1+(1-T_r)^{\frac{2}{7}}} \quad (1.13)$$

Yamada & Gunn (1973)

$$V_{sat} = V_c (0.29056 - 0.08775w)^{(1-T_r)^{\frac{2}{7}}} \quad (1.14)$$

Modified Yamada & Gunn (1973)

$$V_{sat} = \frac{RT_c}{P_c} (0.29056 - 0.08775w)^{1+(1-T_r)^{\frac{2}{7}}} \quad (1.15)$$

Daubert (1997)

$$V_{sat} = \frac{B^{1+(1-\frac{T}{T_c})^D}}{A} \quad (1.16)$$

Hankinson & Thomson (1979)

$$V_{sat} = V_0 * V_1 * (1 - w_{srk} * V_2) \quad (1.17)$$

$$w_{srk} \approx w$$

$$V_0 \approx V_c$$

$$V_1 = 1 + a(1 - T_r)^{\frac{1}{3}} + b(1 - T_r)^{\frac{2}{3}} + c(1 - T_r) + d(1 - T_r)^{\frac{4}{3}}$$

$$V_2 = \frac{e + fT_r + gT_r^2 + hT_r^3}{T_r - 1.00001}$$

a	-1.52816	e	-0.296123
b	1.43907	f	0.386914
c	-0.81446	g	-0.0427258
d	0.190454	h	-0.0480645

SPECIAL CASE ... NORMAL BOILING POINT (i.e.  $P = P_{atm}$  &  $T = T_b$ )

Tyn & Calus (1975)

$$V_{sat} = 0.285V_c^{1.048} \quad (1.18)$$

NOTES ::

- Daubert gives closest approximation if constants are available.
- Modified Yamada & Gunn (1973) does not predict  $V_c$  accurately which implies large errors in values.

Compound	T.C.	Daubert	Rackett	Mod. Rackett	Y.G.	Mod. Y.G.	H.T.
Methane	35.03	37.90	37.23	37.21	37.58	38.03	37.53
n-Heptane	163.15	163.00	163.37	163.31	162.85	162.08	163.19
Ethylene	47.18	49.20	49.32	49.26	49.58	49.86	49.53
Benzene	96.38	95.80	96.81	96.67	97.11	97.38	97.17
Methanol	42.28	42.70	39.28	39.25	41.46	44.58	41.72
Acetone	76.98	77.60	70.92	71.06	77.72	88.12	77.86
Acetic Acid	65.71	66.00	57.32	57.26	64.85	76.62	65.13
Chlorine	44.54	45.40	43.77	42.09	46.28	47.77	46.23
Ammonia	25.38	25.00	24.15	24.11	26.17	28.97	26.20
Water	19.33	18.80	17.65	17.64	19.51	22.16	19.56

Table 1.1: Molar volume of saturated liquids at normal boiling temperatures calculated by Vsat.m

## 1.2.2 Saturated Vapor Pressure

Numerous techniques are available to estimate the saturated vapor pressure as a function of temperature. The following algorithms were programmed into Psat.m

Clausius-Claperyon

$$\ln(P_{sat}) = A - \frac{B}{T} \quad (1.19)$$

Modified Clausius-Claperyon

$$\ln(P_{sat_r}) = h \left(1 - \frac{1}{T_r}\right) \quad (1.20)$$

$$h = \frac{T_{b_r} * \ln\left(\frac{P_c}{P_{atm}}\right)}{(1 - T_{b_r})}$$

Antoine (1888)

$$\ln(P_{sat}) = A - \frac{B}{T + C} \quad (1.21)$$

Wagner (1973) i.e. Wagner 3-6

$$\ln(P_{sat}) = \frac{A\tau + B\tau^{1.5} + C\tau^3 + D\tau^6}{T_r} \quad (1.22)$$

$$\tau = 1 - T_r$$

Wagner (1977) i.e. Wagner 2-5

$$\ln(P_{sat}) = \frac{A\tau + B\tau^{1.5} + C\tau^{2.5} + D\tau^5}{T_r} \quad (1.23)$$

$$\tau = 1 - T_r$$

Riedel (1954)

$$\ln(P_{sat}) = A + \frac{B}{T} + C\ln(T) + DT^6 \quad (1.24)$$

$$A = -35Q$$

$$B = -36Q$$

$$C = 42Q + \alpha$$

$$D = -Q$$

$$Q = K(3.758 - \alpha)$$

$$K = 0.0838$$

$$\alpha = \frac{3.758K\psi + \ln\left(\frac{P_c}{P_{atm}}\right)}{K\psi - \ln(T_{b_r})}$$

$$\psi = -35 + \frac{36}{T_{b_r}} + 42\ln(T_{b_r}) - T_{b_r}^6$$

Modified Riedel - DIPPR

$$\ln(P_{sat}) = A + \frac{B}{T} + C\ln(T) + D * T^E \quad (1.25)$$

Modified Riedel - API

$$\ln(P_{sat}) = A + \frac{B}{T} + C\ln(T) + D * T^2 + \frac{E}{T^2} \quad (1.26)$$

Lee-Kelser

$$\ln(P_{sat_r}) = \ln(P_{sat_r})_0 + w\ln(P_{sat_r})_1 \quad (1.27)$$

$$\ln(P_{sat_r})_0 = 5.92714 - \frac{6.09648}{T_r} - 1.28862\ln(T_r) + 0.169347T_r^6$$

$$\ln(P_{sat_r})_1 = 15.2518 - \frac{15.6875}{T_r} - 13.4721\ln(T_r) + 0.43577T_r^6$$

Ambrose-Walton (1989)

$$\ln(P_{sat_r}) = f_0 + wf_1 + w^2f_2 \quad (1.28)$$

$$f_0 = \frac{-5.97616\tau + 1.29874\tau^{1.5} - 0.60394\tau^{2.5} - 1.06841\tau^5}{T_r}$$

$$f_1 = \frac{-5.03365\tau + 1.11505\tau^{1.5} - 5.41217\tau^{2.5} - 7.46628\tau^5}{T_r}$$

$$f_2 = \frac{-0.64771\tau + 2.41539\tau^{1.5} - 4.26979\tau^{2.5} - 3.25259\tau^5}{T_r}$$
$$\tau = 1 - T_r$$

NOTES ::

- Ambrose-Walton (1989) & Lee-Kelser are applicable to normal, simple compounds (i.e. alkanes, diatomics, etc.). Recommend use of Ambrose-Walton over Lee-Kelser.
- Riedel (1954) not valid for alcohols or acids without modification.
- Two versions of modified Riedel equations exist: one describing the DIPPR database & one describing the API database.
- Modified Riedel - DIPPR data in Perry's Chemical Engineering Handbook
- Antoine (1888) data in Lange's Handbook of Chemistry.



## Chapter 2

# Transport Phenomena

UNDER CONSTRUCTION !!!

# Bibliography

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