POLITECNICO DI TORINO

Department of Environment, Land and Infrastructure Engineering
Master of Science in Petroleum Engineering

Equation of state for hydrocarbons and water

Supervisor:
Prof. Dario Viberti

Co-Supervisor:
Prof. Eloisa Salina Borello

Candidate:

Mostafa Mohamed Elmetwalli Elhawwari [S260872]

July 2020

Acknowledgement

Praise be to allah to complete my thesis as well as my master degree.
First of all, i am grateful for Politecnico di Torino for giving me the opportunity to complete my master studies in outstanding learning environment. I would like to express my deepest appreciation to my supervisor Prof. Dario Viberti, whom I consider as a role model, for his continuous support and guidance during the whole Master of Science program, furthermore for his flexibility and collaboration in the hard days during the global pandemic Covid-19. I would like to extend my sincere thanks to my co-supervisor Prof. Eloisa Salina Borello for her time that she dedicated to help me.

I would like warmly to thank my mom, dad and my siblings for believing in me and for their love and everlasting support during all the stages of my life. Moreover, I’m deeply indebted to my lovely fiancée for her encouragement as well as being always by my side.

Finally, special thanks for my colleagues and friends from whom i get a lot of support during my study time.

Abstract

Reservoir fluids consist mainly in multicomponent system of hydrocarbons, non-hydrocarbons and formation water. Therefore, the reservoir fluids chemical composition is in many cases complex. Analytical equation of state (EOS) is used to calculate the volumetric and phase behavior of the reservoir fluids.

EOS starts from simple ideal gas equation by Émile Clapeyron in 1834, but it had a lot of limitations regarding it’s applicability at real reservoir conditions. As van der Waals (1873) introduced his equation of state, it used to generalize the ideal gas law based on the fact that gases behave as real gases, even it doesn’t have any practical applications nowadays it was considered the basis for revolution in developing and enhancing EOS. In Redlich and Kwong (RK, 1949) equation they included the temperature of the system to the van der Waals attraction term to consider its effects on the intermolecular attractive forces among the atoms which has improved the equation accuracy but it was not the last possible improvements to the VdW equation of state, the Soave-RK (1972) EOS was born as modification on RK EOS with a very good potential as it had overcome the fact that the RK equation was not accurate to express the effect of temperature which in turn improved the application of the equation of state to multicomponent vapor-liquid equilibrium (VLE) calculations. Then, Peng and Robinson (PR, 1976) improved the ability of the equation of state for prediction of densities of liquid and other fluid properties, particularly near the critical zone. Finally, Peneloux et al. (1982) introduced a way to improve the volume predictions for the two parameter SRK EOS by using a volume correction factor, similarly Jhaveri and Youngren (1984) used volume correction factor for the two parameter PR EOS.

Furthermore, for water and by using Tait equation (1888) which is considered one of the most famous empirical equations of state for water along with its modified versions by Tammann (1911) and Gibson (1935). Which is used to correlate volume of liquid to pressure and where B and C are Tait equation parameters. The C parameter was found by Gibson and Loeffier (1941) and equal to (0.3150 x V_o) while many attempts aimed to discover B for water and B* for sea water. It was found that the most internally consistent PVT data on water compared to the Tait equation are the values of Amagat (1893) and Ekman (1908).

Table of Contents

Index of Figures…………………………………………………………………...4

Index of Tables……………………………………………………………………5

List of Abbreviations..6

List of Symbols..6

Chapter 1: Introduction..8

1.1 Equation of state for hydrocarbons...8

1.2 Equation of state for water...9

Chapter 2: Equation of State for Hydrocarbons………………………………..10

2.1 Ideal gas equation…………………………………………………………10

2.2 The Van der Waals Equation of State “VdW EOS”……………………………..13

2.3 Redlich-Kwong Equation of State “RK EOS”……………………………………17

2.4 Soave-Redlich-Kwong Equation of State “SRK2 EOS”………………………...19

2.5 Peng and Robinson Equation of State “PR2 EOS”……………………………...28

2.6 Modifications on SRK EOS (three parameters) “SRK3 EOS”…………………32

2.7 Modifications on PR EOS (three parameters) “PR3 EOS”……………………..34

Chapter 3: Equation of State for Water………………………………………......36

3.1 Tait equation…………………………………………………………………...36

3.2 B calculations for pure water…………………………………………………..38

3.3 B* calculations for sea water………………………………………………......44

3.4 Murnaghan equation of state……………………………………………......49

Chapter 4: Conclusion…………………………………………………………….51

References……………………………………………………………………….....53

Appendix A: Conversion tables……………………………………………………..56

Index of Figure

Figure 1: The Standing and Katz, (1941) chart……………………………………12
Figure 2: Departure of gases from ideal behavior, (Zumdahl, S. S., & Zumdahl, S. A., 2007)…………………………………………………………………………..16
Figure 3: Phase diagram for a pure substance, (Ahmed, T., 2016)…………………..16
Figure 4: $\alpha_i(T)$ obtained against T_{ri} and $\alpha^{0.5}$ against $T_{ri}^{0.5}$, (Soave, 1993)……..…....22
Figure 5: Results obtained for the binary n-butane/methane at 100°F, (Soave, 1972)…………………………………………………………………26
Figure 6: Results for the binary n-decane /methane, (Soave, 1972)………………...27
Figure 7: Results for hydrogen-containing mixtures, (Soave, 1972)………………...27
Figure 8: Results for systems containing hydrogen sulfide, carbon dioxide and polar compounds, (Soave, 1972)……………….……………..………………………28
Figure 9: Results for the binary system carbon dioxide/ isobutane, (Besserer and Robinson, 1973)…………………………….…………………………...……….…32
Figure 10: B of water as a function of temperature, (Yuan-Hui Li, 1967)……...…..41
Figure 11: B* as a function of salinity, (Yuan-Hui Li, 1967)…………………...…...47
Figure 12: B* as a function of salinity and temperature, (Yuan-Hui Li, 1967)….......48

Index of Tables

Table 1: α (0.7) value, (Soave, 1972)……………………………………………...23

Table 2: comparison between root mean square deviation of RK and SRK, (Soave, 1972)……………………………………………………………………………….23

Table 3: calculation of the volume correction parameter for PR and SRK EOS by (Whitson and Brule, 2000) ……………….……………………………….……35

Table 4: Values of d, e suggested by (Jhaveri and Youngren, 1984)……………….....35

Table 5: B of Water Calculated from Data of Amagat (1893) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967)....……….……………………………………...39

Table 6: B of Water Calculated from Data of Amagat (1893) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967).…………………………………………….…40

Table 7: B of Water Calculated from Data of Kennedy (1958) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967)………………….…………...………….…...40

Table 8: B of Water determined from Newton and Kennedy Data (1965) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967)...…...………………….……………...41

Table 9: B of Water determined from Ekman Data (1908) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967)……...………………..……………….…..42

Table 10: B of Water determined from Diaz pena and McGlashan Data (1959) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967)………………..…...…………….…...43

Table 11: B* of sea Water determined from Ekman Data (1908), (Yuan-Hui Li, 1967)………………………………………………………………………………..45

Table 12: B*, $\psi_1$and ψ_2 for Sea Water, (Yuan-Hui Li, 1967)……….…………….……..48

Table 13: n Value of Murnaghan Equation for Ekman's PVT Data of Water β_o from M. Diaz Pena and M. L. McGlashan (1959), (Yuan-Hui Li, 1967).………………......50

Table 14: n Value of Murnaghan Equation for Ekman's PVT Data (1908) of Water β_o from sound velocity data, (Yuan-Hui Li, 1967)………..…...……..…………………...50

List of Abbreviations

EOS	Equation of state.
VdW EOS	Van der Waals Equation of State.
RK EOS	Redlich-Kwong Equation of State.
SRK2 EOS	Soave-Redlich-Kwong Equation of State (2 parameters).
PR2 EOS	Peng and Robinson Equation of State (2 parameters).
SRK3 EOS	Soave-Redlich-Kwong Equation of State (3 parameters).
PR3 EOS	Peng and Robinson Equation of State (3 parameters).
VLE	Vapor-liquid equilibrium.
PCS	Principle of corresponding states.
PVT	Pressure, volume, temperature.
PVTS	Pressure, volume, temperature, salinity.

List of Symbols

P	Pressure	(Pa)
V	Volume	(m^3)
T	Temperature	(K)
n	Number of moles	(-)
R	Universal gas constant = 8.3145	($m^3 \cdot Pa \cdot K^{-1} \cdot mol^{-1}$)
b	Covolume to reflect the volume of molecules	(m^3)
a	Attraction parameter	(-)
P_c	Critical pressure	(Pa)
T_c	Critical temperature	(K)
Z	Compressibility factor	(-)
P_r	Reduced pressure	(-)
T_r	Reduced temperature	(-)
P_{pc}	Pseudo critical pressure	(Pa)
T_{pc}	Pseudo critical temperature	(K)
V_c	Critical volume	(m^3)

Z_l	Compressibility factor for liquid phase	(-)
Z_v	Compressibility factor for gas phase	(-)
Z_c	Critical compressibility factor	(-)
ω	Acentric factor	(-)
β	Isothermal compressibilty of substance	(bar^{-1})
V_o	Specific volume at P=Po= 1 bar	(m^3/kg)
K_o	Bulk compressibility of a substance	(-)
β_s	Adiabatic compressibilty of substance	(bar^{-1})
μ	Velocity of sound	(cm/sec)
S	Shift parameter	(-)

Chapter 1: Introduction

1.1 Equation of state for hydrocarbons

The reservoir fluids consist mainly in multicomponent system of hydrocarbons, non-hydrocarbons and aqueous solutions with dissolved salts (formation water). In all cases composition of the fluids depends on their source, history and present thermodynamic conditions. Hydrocarbons in a reservoir can start from methane with one carbon atom to a very complex compounds containing up to hundred carbon atoms while the most common non-hydrocarbon elements in a reservoir are sulfur, nitrogen and oxygen which can form various types of compounds (non-hydrocarbons are found as a minority). Therefore the reservoir fluids chemical composition is in many cases complex. The volumetric behavior under different thermodynamic conditions of a fluid, single or a multi-component can be calculated and represented adopting a reliable equation of state (EOS). The equation of state is an analytical formula that relates pressure (P), temperature (T) and volume (V), therefore referred as PVT behavior of a single or multicomponent system. EOS is essential relationship to calculate the volumetric and phase behavior of fluids in reservoir and to predict the performance of surface facilities for separation process. Generally, equations of state need the acentric factor for individual components and critical properties, which can be later extended for mixtures. The basic advantage for utilizing an EOS is that with the same equation it could be applied for modeling the behavior of all the phases, while maintaining consistency during doing calculations for phase equilibrium.

EOS starts from simple ideal gas equation by Émile Clapeyron in 1834. However, a lot of limitations regarding the applicability of this equation have led to many trials to have an equation of state more suitable and accurate for description for the behavior of real reservoir fluids at wide range of temperatures and pressures.

Then, as van der Waals (1873) introduced his equation of state, it was considered the basis for revolution in developing and enhancing EOS.

Nowadays, some popular EOS are used in reservoir simulation processes due to their reliability and accuracy in calculation of reservoir fluids properties. A review for some common used EOS in the oil and gas industry will be provided. The Redlich-Kwong

(RK, 1949), Soave-Redlich-Kwong (SRK, 1972) and Peng and Robinson (PR, 1976) equations of state will be discussed considering their strengths and weaknesses and to show their prediction abilities.

Moreover through the review, Peneloux et al. (1982), Jhaveri and Youngren (1984) did a modification on the two parameter SRK, PR equations of state respectively by adding volume shift parameter in order to improve their accuracy, to be called three parameter equations of state.

Basically, many of the trials to improve the accuracy and performance of equation of state took place in the field of empirical cubic equations.

1.2 Equation of state for water

Formation water naturally exists underground in most of the formation and layers, before starting drilling operations. This water is associated with the reservoir fluids gas and oil in different forms (free phase or dissolved). So, it was important to study the water behavior at reservoir condition, to have an idea about the phase behavior of water under range of different temperature, pressure and salinity.

Tait equation (1888) is considered one of the most famous empirical equations of state for water along with its modified versions by Tammann (1911) and Gibson (1935). Which is used to correlate volume of liquid to pressure, B and C are Tait equation parameters which are temperature functions and independent of pressure, the C parameter was found by Gibson and Loeffier (1941) and equal to (0.3150 x V_o) while many attempts aimed to discover B for water and B* for sea water. Mainly B calculations were made by Amagat (1893), Kennedy (1958), Newton and Kennedy (1965), Ekman's bulk compression data (1908), Diaz Pena and McGlashan (1959), Wilson sound velocity data (1960) while B* calculations were carried out by Ekman's bulk compression data (1908), Newton and Kennedy (1965) and sound velocity data by Del grosso (1952), Wilson (1960).

Chapter 2: Equation of State for Hydrocarbons

2.1 Ideal gas equation

The ideal gas equation is considered the first equation of state for describing a hypothetical ideal gas. It could be considered initially a good approximation of many gases behavior under wide range of conditions; nevertheless it has many disadvantages and limitations. It was found by Émile Clapeyron in 1834 as a result of combination between the Charles's law, Boyle's law, Gay-Lussac's law and Avogadro's law (Lim, A.K., 2019).

The ideal gas is known as a gas through which all collisions between atoms or molecules are completely elastic and in which between the atoms there are no intermolecular attractive forces. Atoms could be simulated as solid spheres which collide but without interaction between each other. In the ideal gas, we can find the internal energy in the form of kinetic energy and any variation in the content of internal energy will be associated with a temperature change.

The ideal gas could be described by three different parameters: pressure (P), temperature (T) and volume (V). The mathematical formula that connects them can be evaluated from the kinetic theory which known as the Ideal gas law, which could be written as:

$$PV = nRT \text{ [2.1]}$$

where:

P = pressure of system in Pascal.

T= absolute temperature of system in Kelvin.

R= universal gas constant=8.3144 $m^3 \cdot Pa \cdot K^{-1} \cdot mol^{-1}$

V= volume in m^3

n = number of moles

The ideal gas equation has two main assumptions:

- There are no repulsion or attraction forces among the particles one other.
- The gas atoms volume is negligible in comparison with the total volume of container and to the separation distance between the atoms.

At low pressure or high temperature, the ideal gas law is precise to determine the gas behavior. Moreover, the ideal gas law can’t be used for gases in a reservoir with temperature and pressure extremely higher than atmospheric normal conditions (ideal gas law does not work well at very low temperatures or extremely high pressures, where the gases shows deviations from the ideal behavior, see Figure 2). So, the real gas equation will introduce a compressibility factor (Z) for correction for the ideal gas equation to be able to describe the real gas, which could be written as:

$$PV = ZnRT$$

where Z is the compressibility factor which equal to 1 in case of ideal gas.

The compressibility factor (Z) is a function in pressure, temperature and gas composition. At the reservoir condition, gas is found as a mixture of several gas molecules. Therefore, to calculate the compressibility factor for a mixture, the principle of corresponding states by Van der Waals (1873) could be utilized to evaluate gases under reservoir conditions. The main idea of the principle of corresponding states state that if we used the reduced form for equation of state of gases it will be the same for different types of gas and for different mixtures. The reduced formulas can be described as:

Reduced temperature $\mathrm{T_r = T/T_c}$

Reduced pressure $\mathrm{P_r = P/P_c}$

where:

T_c is the critical temperature.

P_c is the critical pressure.

The critical point is found where the vapor and liquid have the identical properties, and their value is unique for each component.

While in case of gas mixtures, the pseudo reduced properties used to allow dealing with different gas mixtures and compositions which can be expressed as:

Pseudo reduced temperature, $\mathrm{T_{pr} = T/T_{pc}}$

Pseudo reduced pressure, $\mathrm{P_{pr} = P/P_{pc}}$

where:

T_{pc} is the pseudo critical temperature.

P_{pc} is the pseudo critical pressure.

In order to calculate the pseudo critical Pressure and Temperature, the Kay's Rules (Kay, W.B., 1936), could be used as the sum of the weighted average of critical pressure and temperature for each single component in the mixture.

$T_{pc} = y_1 T_{c1} + y_2 T_{c2} + \ldots$

$P_{pc} = y_1 P_{c1} + y_2 P_{c2} + \ldots$

where: y_1, y_2, y_3 are mole fraction for each component.

The Standing and Katz (1941) chart, Figure 1, is used usually for estimation of gas compressibility factor (Z). While the pseudo reduced pressure is on the X-axis and each line inside the chart indicates a value for pseudo reduce temperature. The compressibility factor (Z) is indicated on the Y-axis.

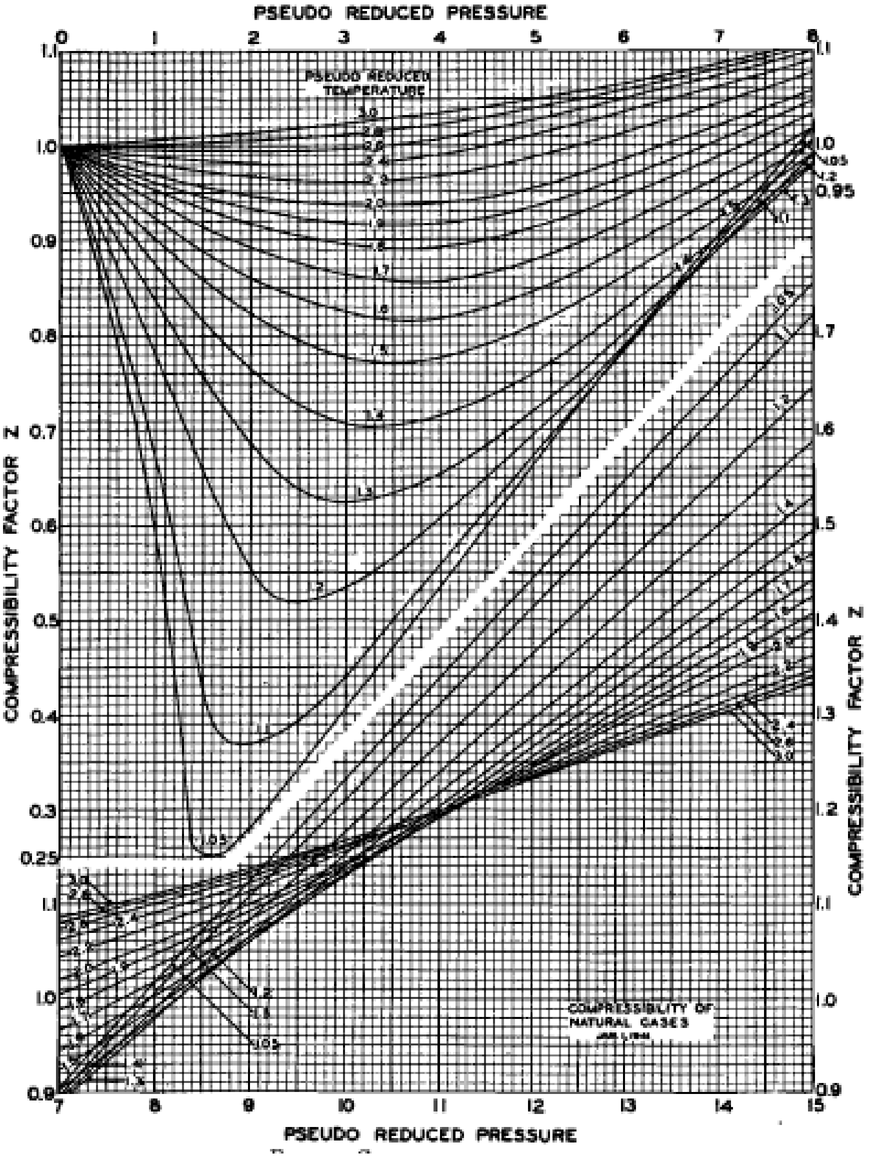


Figure 1: The Standing and Katz, (1941) chart

2.2 The Van der Waals Equation of State "VdW EOS"

The van der Waals (VdW) equation is an equation of state that used to generalize the ideal gas law based on reasonable reasons like that the real gases act in non-ideal way. The ideal gas law deals with molecules of gas as a point particles that interact with their containers yet nothing between one another, this mean that they don't occupy space or even change in kinetic energy during collisions as expressed in the ideal gas law Eq. [2.1] (Ahmed, T., 2016).

Figure 2 shows the deviation of behavior of real gas from ideality for some gases.
Van der Waals (1873) tried to overcome the two assumptions of ideal gas law in order to develop an empirical EOS that can be used for the case of real gas. In his trial to overcome the first assumption, VdW found that the molecules of the gas occupy a large portion of the total volume when pressures is high and he suggested that this is the molecule's volume, which can be indicated by the term b, which must be deducted from the actual volume, in Eq. [2.1], to be as following:

$$P = \frac{RT}{V-b} \quad [2.2]$$

he proposed that the parameter b can be called the covolume and considered to indicate molecule's volume. Where V indicates the actual volume of 1 mol of gas in m^3.
Then for elimination of the second assumption, van der Waals proposed to subtract a correction term, indicated as a/V^2, from this equation to consider the effect of the attractive forces between atoms. Mathematically, van der Waals presented this formula:

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad [2.3]$$

where:
b= repulsion parameter.
a= attraction parameter.
This two parameters, (a) and (b), are constants and used to characterize the molecular properties for single components. The term (a) is assumed to represent the intermolecular attraction forces between the atoms each other while the term (b) represents the volume occupied by the gas particles.

Eq. [2.3] indicates some important characteristics, at low pressures; the gas phase volume is large compared with the molecule's volume. So, the term b is negligible when compared with V and the attractive force term a/V^2 turn to be negligible. So, the VdW EOS goes back to the original ideal gas equation.

At high pressure as (P→ ∞) the volume, V, tend to be extremely small and will have almost the same value of b, which is the actual molecular volume, it can be expressed as:

$$\lim_{P \to \infty} V(P) = b$$

van der Waals EOS or any other type of equation of state could be represented in a more general formula:

$$P = P_{repulsion} - P_{attraction}$$

the repulsion pressure term, $P_{repulsion}$, is defined by the term $\frac{RT}{V-b}$ while the attraction pressure term, $P_{attraction}$, is represented by a/V^2.

To determine the values of (a) and (b), for pure substances, van der Waals realized that the critical isotherm has an inflection point and a horizontal slope at the critical point, and can be calculated as:

$$a = \Omega_a \frac{R^2 T_c^2}{P_c} \quad [2.4]$$

$$b = \Omega_b \frac{R T_c}{P_c} \quad [2.5]$$

where:

T_c= the critical temperature in K.

P_c= the critical pressure in pa.

Ω_a= 0.421875

Ω_b= 0.125

Eq. [2.3] could be written in a cubic form in terms of the volume "V" as follows:

$$V^3 - \left(b + \frac{RT}{P}\right) V^2 + \left(\frac{a}{P}\right) V - \left(\frac{ab}{P}\right) = 0 \quad [2.6]$$

Eq. [2.6] could be described as two parameter cubic equation of state of van der Waals. Where the two parameter term indicates the two parameters (a) and (b), while the cubic equation of state term indicates that there are three solutions of the equation in terms of volume V, in which at least one of them is real.

One of the important aspects of Eq. [2.6] that it can depict the condensation phenomenon of liquid and the transformation from the gas phase to the liquid phase by pressurizing the gas. These significant aspects of VdW EOS are explained through Figure 3.

"Assume we have a pure substance with a PV behavior as represented in Figure 3, while assuming that the substance is kept under it's critical temperature (constant). Taking into account this temperature, Eq. [2.6] will have 3 solutions in terms of volumes for each value of pressure, P. At constant temperature a solution, is indicated graphically by the dashed isotherm, which is the constant temperature curve "BZEWD". The possible 3 values of volume are the intersections of B, D, and E with the horizontal line, which corresponds to only one pressure value. The determined dash line "BZEWD" will represent the continuous transformation of gas phase to liquid phase; while actually, the transformation is discontinuous and abrupt, for both vapor and liquid falling on the horizontal line "BD". By checking the graphical solution for Eq. [2.6] (see Figure 3) indicates that the smallest positive volume, represented by point B, corresponds to the saturated liquid volume while the largest solution root (volume), which is represented by point D, corresponds to the volume of the saturated vapor. The third root, represented by point B, is physically meaningless" (Ahmed, T., 2016).

It can be noticed that these values will be the same at temperature near the critical temperature T_c for any substance.

Eq. [2.6] could be also expressed in terms of the compressibility factor, Z, and by substituting the molar volume V, in Eq. [2.6] by the term, ZRT/p to give:

$$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \left(\frac{a}{P}\right)V - \left(\frac{ab}{P}\right) = 0$$

$$V^3 - \left(b + \frac{RT}{P}\right)\left(\frac{ZRT}{P}\right)^2 + \left(\frac{a}{P}\right)\left(\frac{ZRT}{P}\right) - \left(\frac{ab}{P}\right) = 0$$

to be:

$$Z^3 - (1 + B)Z^2 + AZ - AB = 0 \quad [2.7]$$

where:

$$A = \frac{aP}{R^2T^2} \quad [2.8]$$

$$B = \frac{bP}{RT} \quad [2.9]$$

Eq. [2.7] results in one root solution in the one phase region and three real root solutions in the two phase region. Note that in the two phase region, the smallest positive root gives the compressibility factor for the liquid phase, Zl, while the largest positive root gives the compressibility factor for the vapor phase, Zv.

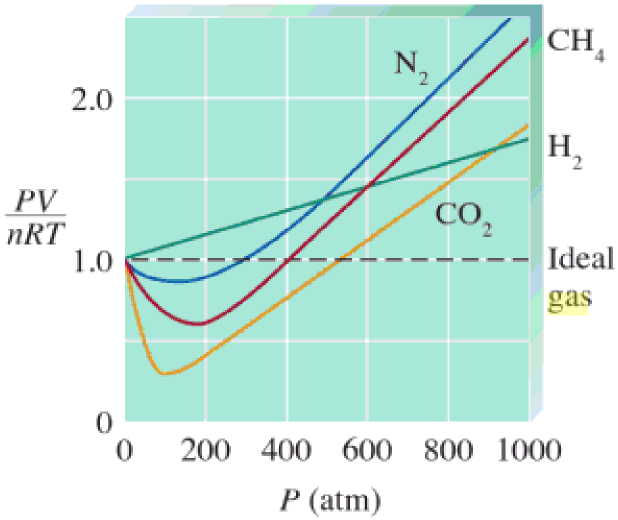


Figure 2: Departure of gases from ideal behavior, (Zumdahl, S. S., & Zumdahl, S. A., 2007).

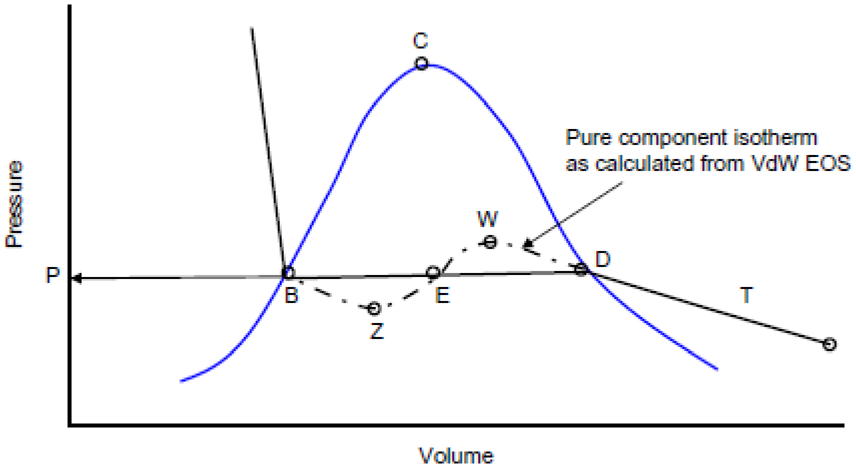


Figure 3: phase diagram for a pure substance, (Ahmed, T., 2016).

Even van der Waals has introduced his equation more than one hundred years ago, VdW EOS considered the basis for revolution in developing and enhancing EOS. VdW EOS is important for many reasons; even it doesn't have any practical usage nowadays. Actually, VdW EOS has no application anymore in design purposes. However, most of the EOS that nowadays used for practical design purposes used VdW EOS as basis for its derivation.

The VdW EOS importance could be summarized in few points:

- Its prediction ability was successfully better than ideal gas EOS.
- It was the first equation that predicts continuous behavior of matter between liquid and gas.
- It helped to formulate the Principle of Corresponding States (PCS).
- It became basis for other developed cubic EOS.

2.3 Redlich-Kwong Equation of State "RK EOS"

According to Redlich and Kwong (RK, 1949) they realized that in the van der Waals term a/V^2 the temperature of the system is not included to take into account its effects on the intermolecular attractive forces among the particles. Redlich and Kwong indicated that by adjusting the van der Waals a/V^2 term to include the temperature of the system can considerably enhance the predictive results of the physical and volumetric properties for the vapor phase (Ahmed, T., 2016). Redlich and Kwong substituted the term of attraction pressure with a general temperature dependent term, which can be expressed as following:

$$P = \frac{RT}{V-b} - \frac{a/T^{0.5}}{V(V+b)} \quad [2.10]$$

where T is the system temperature in K.

The main change they proposed was to the functional form of δP attraction. Furthermore, they add the covolume (b) in the denominator of the functional form. The basic idea is that the attraction parameter (a) of van der Waals wanted to be a temperature dependent before any cubic EOS have the ability to match the experimental data with acceptable degree. VdW himself had proposed this, but no actual work had been done till the work by Redlich Kwong (1949).

Redlich and Kwong realized that, when the pressure of the system increases too much towards (P →∞) the substance molar volume V, decreases to around 26% of its critical volume V_c, without depending on the temperature of the system. So, they expressed Eq. [2.10] in order to satisfy this condition:

$$b = 0.26V_c \quad [2.11]$$

by introducing the critical point conditions to Eq. [2.10] and by solving the two equations simultaneously, gives:

$$a = \Omega_a \frac{R^2 T_c^{2.5}}{P_c} \quad [2.12]$$

$$b = \Omega_b \frac{RT_c}{P_c} \quad [2.13]$$

where:

Ω_a=0.42747

Ω_b=0.08664

it could be noted that by equalizing Eq. [2.11] with [2.13] gives:

$$0.26V_c = \Omega_b \frac{RT_c}{P_c}$$

and by arranging the above expression:

$$P_c V_c = 0.33RT_c \quad [2.14]$$

Eq. [2.14] show that the RK EOS uses a universal critical compressibility factor (Zc) with a value = 0.333 suitable for all the substances. As known, the critical gas compressibility have values which ranges from 0.23 to 0.31 suitable for almost all of the substances, and have an average value= 0.27.

By substituting the molar volume V, in Eq. [2.10] by the term ZRT/P, will result the following equation:

$$Z^3 - (1 + B)Z^2 + AZ - AB = 0 \quad [2.15]$$

where:

$$A = \frac{aP}{R^2 T^{2.5}} \quad [2.16]$$

$$B = \frac{bP}{RT} \quad [2.17]$$

and as in the van der Waals EOS, Eq. [2.15] gives three real root solutions in the two phase zone, and one root solution in the one phase zone (liquid phase region or gas phase region). In the first case, the smallest positive root gives the compressibility factor of the liquid Zl while the highest root gives the compressibility of the gas phase Zv.

The importance of Redlich-Kwong EOS lies in that when a systematic work on EOS started, the only equation of state available that combine simplicity of treatment and exactness was the RK equation, because of its cubic nature it has many useful practical applications, and not like second order equations it can be used for the liquid phases.

Normally, Redlich and Kwong EOS were not the last possible improvements to the VdW equation of state. Actually, the Redlich Kwong EOS is not used anymore for practical applications nowadays. However, the research continued so as to improve the RK EOS. Two decades later, the Soave-RK EOS was born as modification on RK EOS with a very good potential.

2.4 Soave-Redlich-Kwong Equation of State “SRK2 EOS”

The Redlich Kwong (SRK) equation is generally could be regarded as the best two parameter EOS introduced till now (Soave, 1972). As it could be used to determine by acceptable accuracy, thermal and volumetric properties for pure substances as well as mixtures, but its application to multicomponent Vapor-liquid equilibrium (VLE) calculations leads mostly to poor results.

Actually this cannot be related only due to mixing rule imperfection. However, it should be related to the fact that the equation was not accurate to express the effect of temperature.

Actually, the accuracy is not improved if we calculate the vapor pressures for the pure substances, which should not be affected by mixing rules.

The Soave work actually based on the assumption that an enhancement in producing saturation conditions for pure substances will also results in an improvement to that of mixtures. Note that there is acceptable matching among experimental and computed vapor pressures for pure compounds is not necessary enough condition to match that of mixtures also, but at least an important one.

From the original equation of Redlich Kwong [2.10] and by the work done by Soave, the original equation was adjusted by substituting the term $a/T^{0.5}$ with a general temperature dependent term, a (T):

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \quad [2.18]$$

and by assuming:

$$V = \frac{ZRT}{P}$$

$$A = \frac{aP}{R^2T^2} \quad [2.19]$$

$$B = \frac{bP}{RT} \quad [2.20]$$

Eq. [2.18] could be written as following:

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \quad [2.21]$$

starting with Pure Substances and by supposing that, at the critical point, the first and second pressure derivatives with respect to volume be zero, it could be obtained that:

$$a_i(T_{ci}) = a_{ci} = 0.42747\frac{R^2T_{ci}^2}{P_{ci}} \quad [2.22]$$

$$b_i = 0.08664\frac{RT_{ci}}{P_{ci}} \quad [2.23]$$

and at temperatures different from the critical temperature:

$$a_i(T) = a_{ci}\alpha_i(T) \quad [2.24]$$

where $\alpha_i(T)$ is a dimensional factor which is equal to one at T = T_{ci} .

By applying Eqs. [2.22]-[2.23]-[2.24], Eqs. [2.19] and [2.20] become, for pure substances:

$$A = 0.42747\alpha_i(T)\frac{P/P_{ci}}{(T/T_{ci})^2} \quad [2.25]$$

$$B = 0.08664 \frac{P/P_{ci}}{T/T_{ci}} \quad [2.26]$$

the fugacity coefficient for a pure substance could be calculated as:

$$\ln\frac{f}{P} = Z - 1 - \ln(Z - B) - \frac{A}{B}\ln(\frac{Z+B}{Z}) \quad [2.27]$$

the compressibility factor (Z) that utilized in Eq. [2.27] was calculated previously by solving Eq. [2.21] (one or three real roots can be obtained; and for the three roots, the highest one for the vapor phase while the smallest root is for the liquid phase).

For a pure substance and at temperature known and for a known value of a (T), only one value of P exists which fulfills the saturation condition:

$$f_i^L = f_i^V \quad [2.28]$$

to calculate this pressure we use trial and error, and for each pressure value solving two times Eq. [2.21], one time for the vapor phase and other time for the liquid phase, then by using the two roots into Eq. [2.27]; the correct value of pressure is when the calculated two values $\frac{f}{P}$ are the same.

Reversely, by setting an experimental value for the saturation pressure, Eq. [2.28] is fulfilled by only one value of a (T), that is that of α (T).

So, it is possible to calculate from experimental vapor pressures and for each substance a group of values of α (T).

Which was done for some of hydrocarbons, assuming as experimental vapor pressures the accurate Antoine expressions reported by (API Project 44, 1953).

If we plot $T_{ri} = T/T_{ci}$ against the values of $\alpha_i(T)$ obtained, we will have separate curves, which show similar trends. While if we plot ($\alpha^{0.5}$ versus $T_{ri}^{0.5}$), we will get almost straight lines, (see Figure 4).

Note that all the lines should pass through the same point ($T_r = \alpha = 1$) so, the following expression can be written:

$$\alpha_i^{0.5} = 1 + m_i(1 - T_r^{0.5}) \quad [2.29]$$

the slopes m_i could be related in a direct way with the acentric factors ω_i for different compounds. Actually, each value of the acentric factor ω gives a value of the reduced vapor pressure at a reduced temperature with value = 0.7:

$$P_{ri}^{sat}(T_r = 0.7) = 10^{-1-\omega} \quad [2.30]$$

from $T_r = 0.7$ and $P_r = 10^{-1-\omega}$ we will obtain a value of α_i (0.7), which rely on the supposed values of ω only (see Table 1). Then by forcing all the straight lines, as defined by Eq. [2.29], in order to pass through the points (T_r = 0.7, α = α (0.7)), the following relation was found:

$$m_i = 0.48 + 1.574\omega_i - 0.176\omega_i^2 \quad [2.31]$$

Equations [2.24], [2.29] and [2.31] yield the desired value of a_i (T) for certain substance and at any temperature, while the only values needed are the acentric factor and critical constants (pressure and temperature).

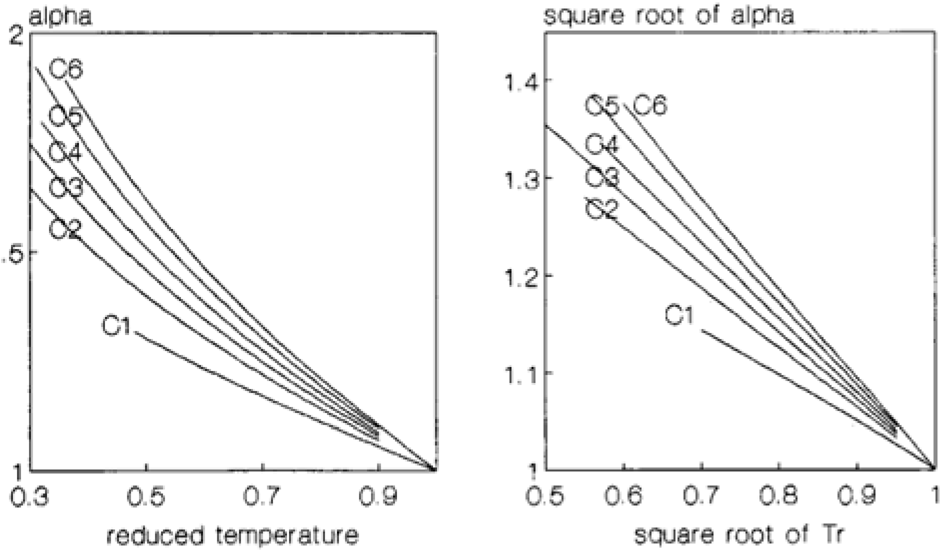
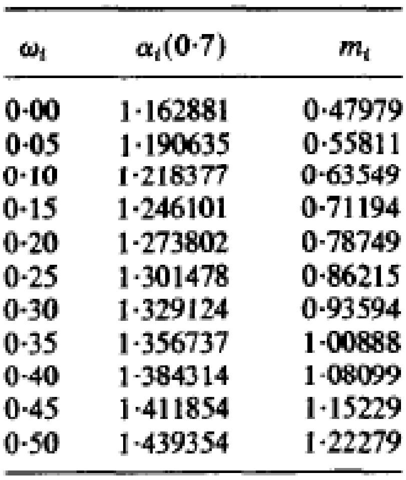


Figure 4: $\alpha_i(T)$ obtained against T_{ri} and $\alpha^{0.5}$ against $T_{ri}^{0.5}$, (Soave, 1993).

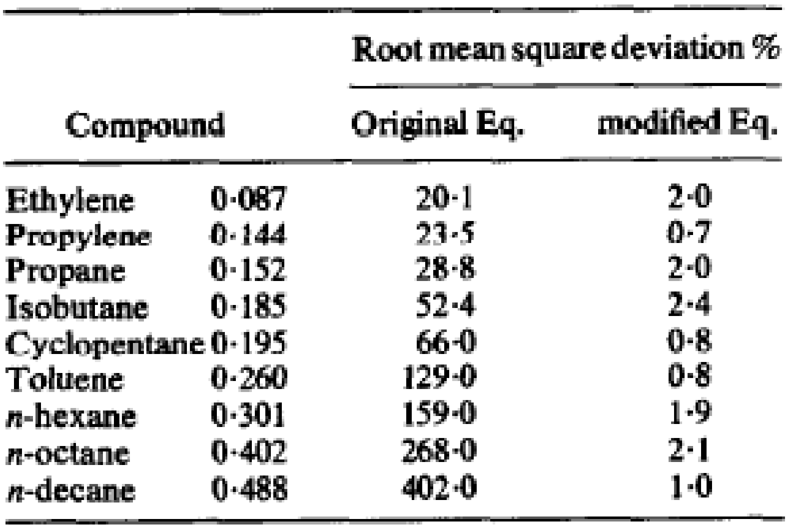


ω_i	$\alpha_i(0·7)$	m_i
0·00	1·162881	0·47979
0·05	1·190635	0·55811
0·10	1·218377	0·63549
0·15	1·246101	0·71194
0·20	1·273802	0·78749
0·25	1·301478	0·86215
0·30	1·329124	0·93594
0·35	1·356737	1·00888
0·40	1·384314	1·08099
0·45	1·411854	1·15229
0·50	1·439354	1·22279

Table 1: α (0.7) values, (Soave, 1972).

To prove whether these modifications are effective or not, the vapor pressures for some hydrocarbons should be calculated then to be compared with the experimental data. Precise acentric factors values were obtained from experimental data, and the same was calculated for the main equation by Redlich-Kwong.

It was found that the main equation gave vapor pressures with high error compared with the values obtained experimentally, especially for substances with high acentric factor values, while SRK equation have good agreement with the experimental values obtained (see Table 2). All the vapor pressures calculated according to SRK equation had small S-shaped deviations, with a possibility to split over at the end of temperatures range tested, which is at reduced temperature smaller than 0.4.



Compound		Root mean square deviation %	
		Original Eq.	modified Eq.
Ethylene	0·087	20·1	2·0
Propylene	0·144	23·5	0·7
Propane	0·152	28·8	2·0
Isobutane	0·185	52·4	2·4
Cyclopentane	0·195	66·0	0·8
Toluene	0·260	129·0	0·8
n-hexane	0·301	159·0	1·9
n-octane	0·402	268·0	2·1
n-decane	0·488	402·0	1·0

Table 2: comparison between root mean square deviation of RK and SRK, (Soave, 1972).

However, there is possibility of further enhancement by using more refined expression for α (T) , especially while treating mixtures that contain very light components, especially hydrogen, which need an extrapolation of α (T_r) to high values of reduced temperatures.

Then, for Mixtures**,** and for simplification, the original mixing rules, tried first:

$$a = (\sum x_i \, a_i^{0.5})^2 \quad [2.32]$$

$$b = \sum x_i b_i \quad [2.33]$$

as a result, it was found that these rules can be used obtaining good results for the non-polar fluids mixtures, like hydrocarbons, carbon monoxide, nitrogen, excluding the hydrogen sulfide and carbon dioxide. With no special deviation to occur in the widely different volatilities mixtures, so as conclusion the above mixing rules are found to be adequate with good accuracy.

With application of mixing rules [2.32] and [2.33] to Eqs. [2.19], [2.20], [2.22] and [2.23], the following expressions could be obtained:

$$A = 0.42747 \frac{P}{T^2} (\sum x_i \, \frac{T_{ci}\alpha_i^{0.5}}{P_{ci}^{0.5}})^2 \quad [2.34]$$

$$B = 0.08664 \frac{P}{T} \sum x_i \, \frac{T_{ci}}{P_{ci}} \quad [2.35]$$

the coefficient of fugacity for a component in the mixture is given by:

$$\ln \frac{f_i}{P_{xi}} = \frac{b_i}{b}(Z-1) - \ln(Z-B) - \frac{A}{B}(2\frac{a_i^{0.5}}{a^{0.5}} - \frac{b_i}{b}) \ln(1+\frac{B}{Z}) \quad [2.36]$$

in which the ratios $\frac{b_i}{b}$ and $\frac{a_i}{a}$ are given by:

$$\frac{a_i^{0.5}}{a^{0.5}} = \frac{\alpha_i^{0.5} T_{ci}/P_{ci}^{0.5}}{\sum x_i \alpha_i^{0.5} T_{ci}/P_{ci}^{0.5}} \quad [2.37]$$

$$\frac{b_i}{b} = \frac{T_{ci}/P_{ci}}{\sum x_i T_{ci}/P_{ci}} \quad [2.38]$$

where the compressibility factor (Z) is computed by resolving the previous Eq. [2.21], (the greatest root is for the vapor phases while the smallest root is for the liquid phase). The previous equations were calculated for some binary systems then the results have to be compared with that obtained from experimental data. While the same was carried out for the original or the main equation.

Figure 5, demonstrates the results that computed for the system n-butane/methane at T=100°F along with the experimental data obtained from (Sage and Lacey, 1950). We can see that the modified equation have good fitting with the experimental data curve, especially for the vapor phase.

Moreover, also the error in calculated bubble pressures for the liquid phase is little. Noting that the determined liquid and vapor curves get together almost at the values of experimental critical pressure and composition. This was found in all the examined cases, then we could have conclusion that the proposed equation has the ability for prediction of the phase behavior for mixtures even in the critical zone.

In order to test the precision of the used mixing rule, some investigations for several binary systems composed by components having various range of volatilities could be done. And for example the result of the system n-decane/methane is shown in Figure 6 .Note that no loss of accuracy is found compared to the first binary system. Furthermore, the same happened for similar cases, so as a conclusion the mixing rules used (the same with the one in the original equation) are acceptable to use.

However, higher deviations were noticed for mixtures having hydrogen (see Figure 7). The classic critical constants of hydrogen were utilized, along with a value= -0.22 for the acentric factor, which is computed from hydrogen experimental vapor pressures. No enhancement is observed when using effective and critical constants. A significant enhancement was noticed, in a certain ranges of pressure (up to 1000/2000 psi), by utilizing a good acentric factor values. Empirical corrections is needed for systems which contain hydrogen sulfide, carbon dioxide, and polar compounds, in which we have large deviations, also the vapor pressures for every pure components were calculated (see Figure 8).

In cases like this we can’t apply the general mixing rules given previously as they suppose that:

$$a_{i\,j} = (a_i a_j)^{1/2} \quad [2.39]$$

in general, we could write:

$$a_{i\,j} = (1 - K_{i\,j})(a_i a_j)^{1/2} \quad [2.40]$$

where K_{ij} is a correction factor (empirical), that can be calculated experimentally, for every binary system found in the mixture (assume n is the number of components in the mixture, the binary systems existed will be n(n-1)/2).

It was indicated that each value of K_i factor could be considered as independent from the temperature of the system, composition and pressure. It is possible that by using these correction factors will help to enhance the results for mixtures with normal components, like hydrogen and hydrocarbons.

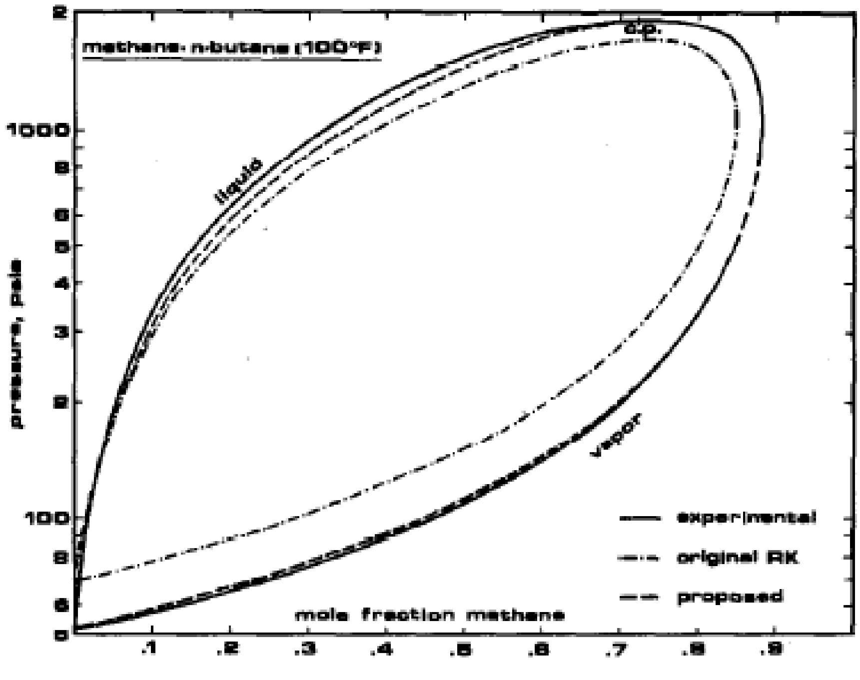


Figure 5: results obtained for the binary n-butane/methane at 100°F, (Soave, 1972).

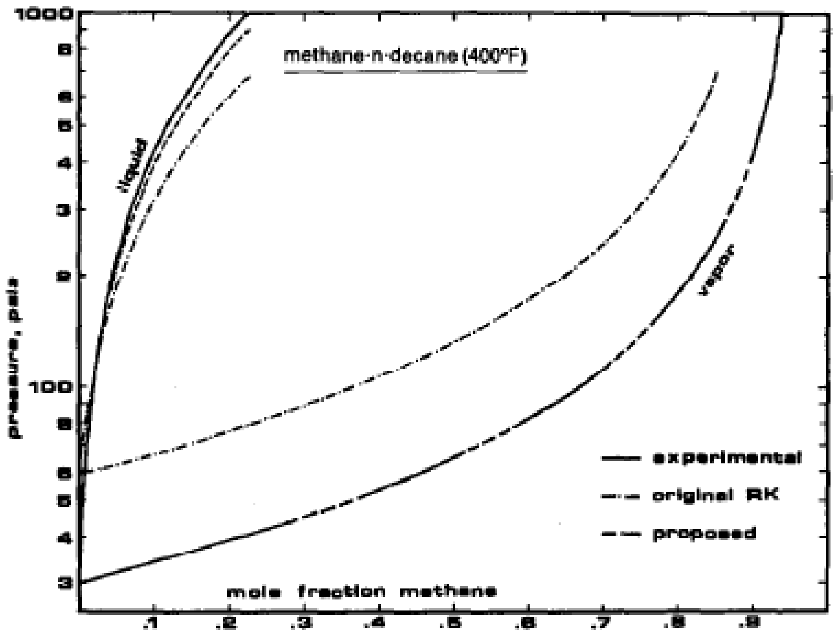


Figure 6: results for the binary n-decane/methane, (Soave, 1972).

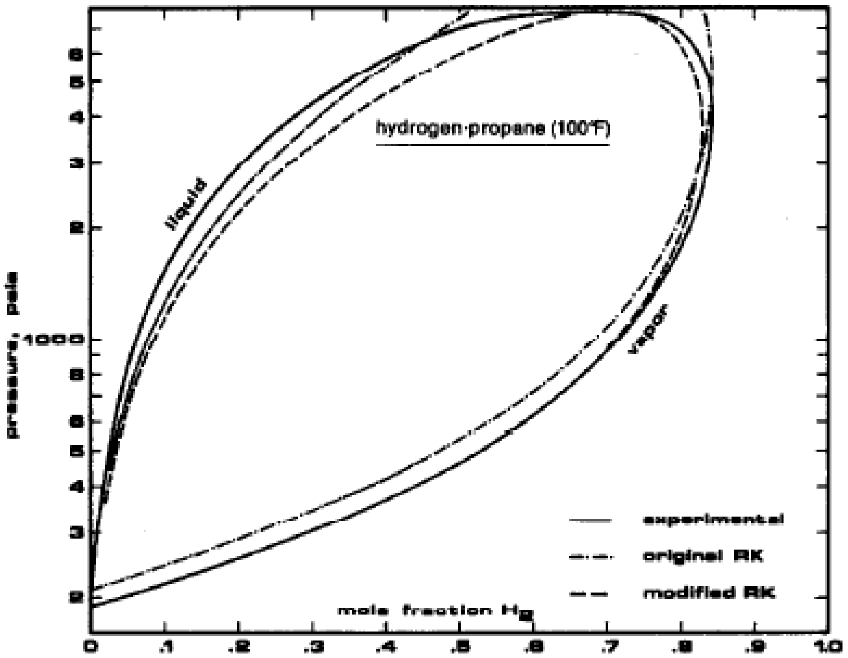


Figure 7: results for hydrogen-containing mixtures, (Soave, 1972).

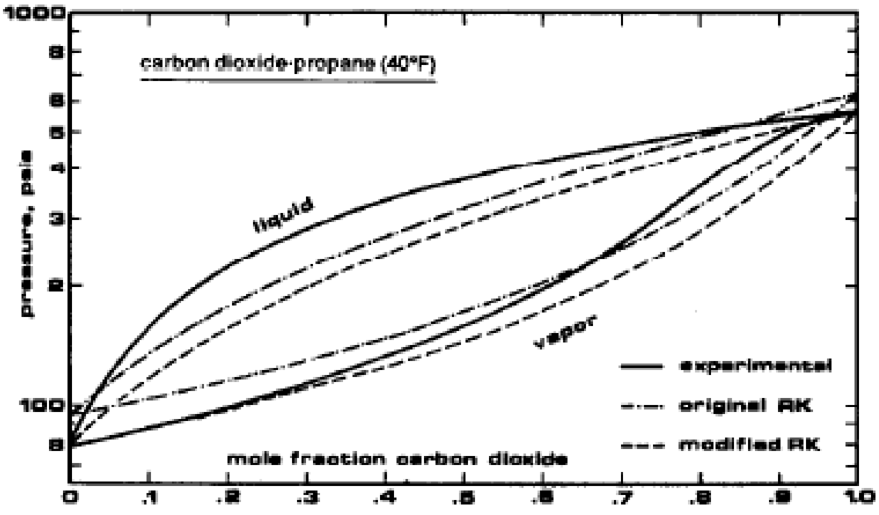


Figure 8: Results for systems containing hydrogen sulfide, carbon dioxide and polar compounds, (Soave, 1972).

2.5 Peng and Robinson Equation of State "PR2 EOS"

Ding-Yu Peng and Donald B. Robinson (PR, 1976) performed a detailed study for evaluation for the usage of the SRK EOS for estimation of hydrocarbon systems behavior. They proved the importance for an improvement to enhance the capability of the equation of state for prediction of densities of liquid and other fluid properties, particularly near the critical zone (Ahmed, T., 2016).

Peng and Robinson, Semi empirical EOS basically expresses the pressure as summation of two terms, attraction pressure P_A and a repulsion pressure P_R as following:

$$P = P_R + P_A \quad [2.41]$$

the equations of VdW (1873), RK (1949), and SRK (1972) all have the repulsion pressure term used by VdW equation, as:

$$P_R = \frac{RT}{V-b} \quad [2.42]$$

while attraction pressure term indicated by:

$$P_A = -\frac{a}{g(v)} \quad [2.43]$$

where g (v) is a function in (b) that is related to the hard spheres size and the molar volume (V), while parameter (a) is related to the intermolecular attraction force. By using Eq. [2.41] at the critical point where the pressure first and second derivatives with respect to volume disappear values for (a) and (b) at the critical point could be computed by using the critical properties. But (b) is considered as non-dependent on temperature. Note that values of (a) are only constant in VdW EOS.

For the RK and SRK equations, scaling factors (dimensionless) can be utilized for describing the temperature dependency for the energy parameter.

From study of the semi empirical equations which have the form as in Eq. [2.41] shows that by selecting an appropriate function for g (v), the predicted value of the critical compressibility factor could be improved to reach a values which is more real. The application of this equation at extremely high pressure ranges is influenced by the value of b/V_c, note that V_c is the critical volume predicted.

Moreover, by confronting RK and SRK equations, it was proved that using the dimensionless scale factor for the energy parameter as a function of acentric factor and by using the reduced temperature has obviously enhanced the vapor pressures estimation for both pure substances and for mixtures.

The equation was proposed as the following:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \quad [2.44]$$

Eq. [2.44] could be rewritten as:

$$Z^3 - (1-B)Z^2 + Z(A - 3B^2 - 2B) - (AB - B^2 - B^3) = 0 \quad [2.45]$$

where:

$$A = \frac{aP}{R^2T^2} \quad [2.46]$$

$$B = \frac{bP}{RT} \quad [2.47]$$

$$Z = \frac{PV}{RT} \quad [2.48]$$

Eq. [2.45] results as before in one or three solutions based on the phase number in the system. For the two phase zone, the smallest positive solution root corresponds to the liquid phase compressibility factor Zl while the largest root is for the vapor phase compressibility factor Zv. By using Eq. [2.44] at the critical point, it could be obtained:

$$a(T_c) = 0.45724\frac{R^2T_c^2}{P_c} \quad [2.49]$$

$$b(T_c) = 0.0778\frac{RT_c}{P_c} \quad [2.50]$$

$$Z_c = 0.307 \quad [2.51]$$

as shown from the results of the previous equation, it gives a universal critical gas compressibility factor Zc = 0.307, compared with a value from SRK= 0.333.

For temperatures different from the critical:

$$a(T) = a(T_c)\alpha(T_r, \omega) \quad [2.52]$$

$$b(T) = b(T_c) \quad [2.53]$$

where $\alpha(T_r, \omega)$ is a dimensionless function of the acentric factor and reduced temperature and equal to one at the critical temperature. Eq. [2.52] is the same utilized by (Soave, 1972) in his modification of RK equation.

The fugacity of a pure component could be written as:

$$\ln\frac{f}{P} = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B}\ln\left(\frac{Z+2.414B}{Z-0.414B}\right) \quad [2.54]$$

the α value is calculated at equilibrium condition

$$f^L = f^V \quad [2.55]$$

is fulfilled along the curve of vapor pressure. With a convergence criterion of $(f^L - f^V) < 10^{-4}$ kPa about 2 to 4 iterations were needed for obtaining a value for α at each temperature.

For all tested substances the relation among T_r and α, Peng and Robinson used Soave's method to calculate the parameter α, as following:

$$\alpha^{0.5} = 1 + k(1 - T_r^{0.5}) \quad [2.56]$$

where k is a characteristic for every substance and it is constant. This constant has been related with the acentric factors, to have:

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad [2.57]$$

Peng and Robinson (1978) suggested this formula for k values that can be used with heavy components with values of acentric factor ω > 0.49:

$$k = 0.379642 + 1.48503\omega - 0.1644\omega^2 + 0.016667\omega^3 \quad [2.58]$$

note that Eq. [2.56] is comparable to that used by Soave (1972) for his modification on RK EOS, also Eq. [2.56] is calculated for every substance by using the data of vapor pressure from boiling point to the critical point while Soave employed the critical point and the computed vapor pressure at $T_r = 0.7$ only, which depend on the acentric factor value.

For mixture, the fugacity coefficient for component k in a mixture could be computed through this expression:

$$\ln\frac{f_k}{x_k P} = \frac{b_k}{b}(Z-1) - \ln(Z-B) - \frac{A}{2\sqrt{2}B}\left(\frac{2\sum X_i a_{i\,k}}{a} - \frac{b_k}{b}\right)\ln\left(\frac{Z+2.414B}{Z-0.414B}\right) \quad [2.59]$$

the mixture parameters were characterized by the mixing rule as:

$$a = \sum_i \sum_j x_i x_j a_{i\,j} \quad [2.60]$$

$$b = \sum x_i b_i \quad [2.61]$$

where:

$$a_{ij} = \left(1 - \delta_{ij}\right) a_i^{0.5} a_j^{0.5} \quad [2.62]$$

in Eq. [2.62] δ_{ij} is an empirical interaction coefficient for a binary system composed of component (i) & (j). Eq. [2.62] used previously by Zudkevitch and Joffe (1970) for their modification on RK equation to calculate equilibrium ratios between vapor and liquid. Note that all δ_{ij} were calculated by using experimental binary VLE data. The value of δ_{ij} calculated for every binary system was the value which has the minimum deviation in the bubble point pressures prediction. The significance of the interaction coefficient is demonstrated in Figure 9 which is for the binary system carbon dioxide/isobutene (Besserer and Robinson, 1973).

It is noted that using of the interaction coefficients has result in improving the estimations.

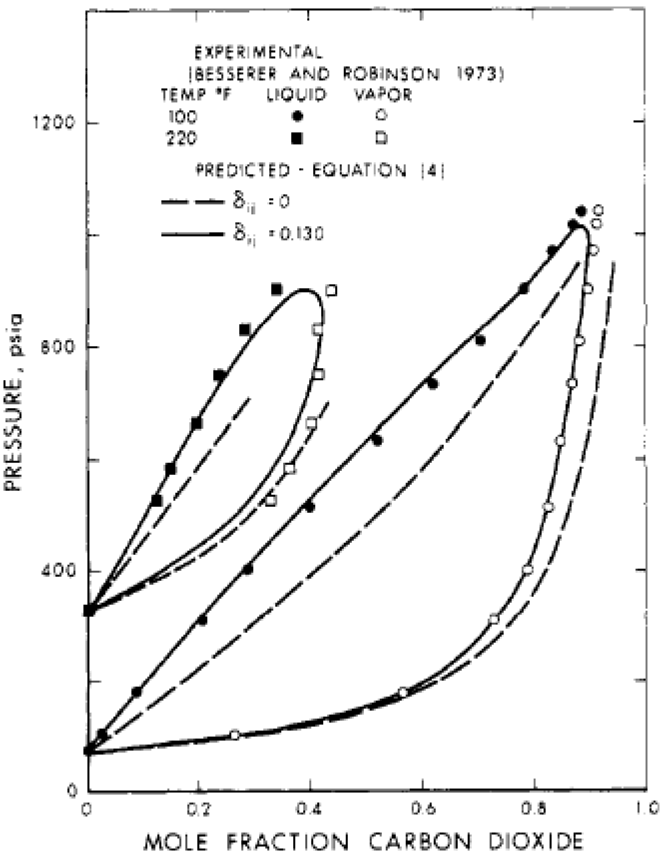


Figure 9: Results for the binary system carbon dioxide/isobutane, (Besserer and Robinson, 1973).

2.6 Modifications on SRK EOS (three parameters) “SRK3 EOS”

The method is based on adding volume shift parameter to enhance the accuracy of the equation of state for estimation of different parameters (Ahmed, T., 2016).

The main disadvantage of SRK2 EOS is that the critical compressibility factor uses unreal universal critical compressibility with value 0.333 for any substances. So, the molar volume is usually overestimated. Therefore, calculated densities tend to be underestimated.

Peneloux et al. (1982) presented a way to enhance the volume forecast for SRK2 EOS by using a volume correction factor, ci, to the original equation. The third parameter will not change the liquid/vapor equilibrium conditions which is calculated by the original not modified SRK equation but it will modify the gas and liquid volumes. Volume translation method will use these formulas:

$$V^L_{corrected} = V^L - \sum_i (x_i c_i) \quad [2.63]$$

$$V^V_{corrected} = V^V - \sum_i (y_i c_i) \quad [2.64]$$

where:

V^V is the not corrected gas volume where $V^V = Z^V RT/P$ in m^3/mol

V^L is the not corrected liquid volume where $V^L = Z^L RT/P$ in m^3/mol

$V^V_{corrected}$ is the corrected gas volume in m^3/mol

$V^L_{corrected}$ is the corrected liquid volume in m^3/mol

y_i is the component (i) mole fraction in the gas phase.

x_i is the component (i) mole fraction in the liquid phase.

It was suggested six methodologies for computing the correction factor, ci, for each single component. For reservoir fluids and for heavy hydrocarbons, Peneloux (1982) proposed that the best parameter to be related with volume correction factor ci is Rackett compressibility factor, Z_{RA}. Mathematically the correction factor can be expressed as following:

$$c_i = 4.437978(0.29441 - Z_{RA}) T_{ci}/P_{ci} \quad [2.65]$$

where:

c_i is the volume shift coefficient for component (i) in m^3/mol

T_{ci} is the component critical temperature in K

p_{ci} is the component critical pressure in Pa

the parameter Z_{RA} is regarded as a constant for every component. Generally, the values of Z_{RA}, have no big difference from the values of the critical compressibility factors, Z_c. But if these values are not available, Peneloux et al. (1982) suggested this relation to determine ci:

$$c_i = (0.0115831168 + 0.411844152\omega_i) T_{ci}/P_{ci} \quad [2.66]$$

where:

ωi = component acentric factor.

2.7 Modifications on PR EOS (three parameters) "PR3 EOS"

Jhaveri and Youngren (1984) figured out that, during application of Peng Robinson EOS (PR2) on reservoir fluids, there is error related to the equation for estimation of gas phase Z factor ranges from 3% to 5% while for liquid density predictions the error ranges from 6% to 12%. Similarly as suggested by Peneloux (1982) in the SRK3 EOS, Jhaveri and Youngren (1984) used volume correction factor, ci, to the PR equation of state. The correction parameter has same units of the parameter, bi, of the not modified PR equation and could be expressed as following:

$$c_i = S_i b_i \quad [2.67]$$

where S_i is the shift parameter, dimensionless parameter, and b_i from Peng Robinson is the co-volume, as indicated in Eq. [2.50].

Similarly to SRK EOS, this volume correction parameter ci, will not affect the liquid/ vapor equilibrium conditions. The corrected volumes of hydrocarbon phases can be expressed as the following:

$$V^L_{corrected} = V^L - \sum_i (x_i c_i) \quad [2.68]$$

$$V^V_{corrected} = V^V - \sum_i (y_i c_i) \quad [2.69]$$

where:

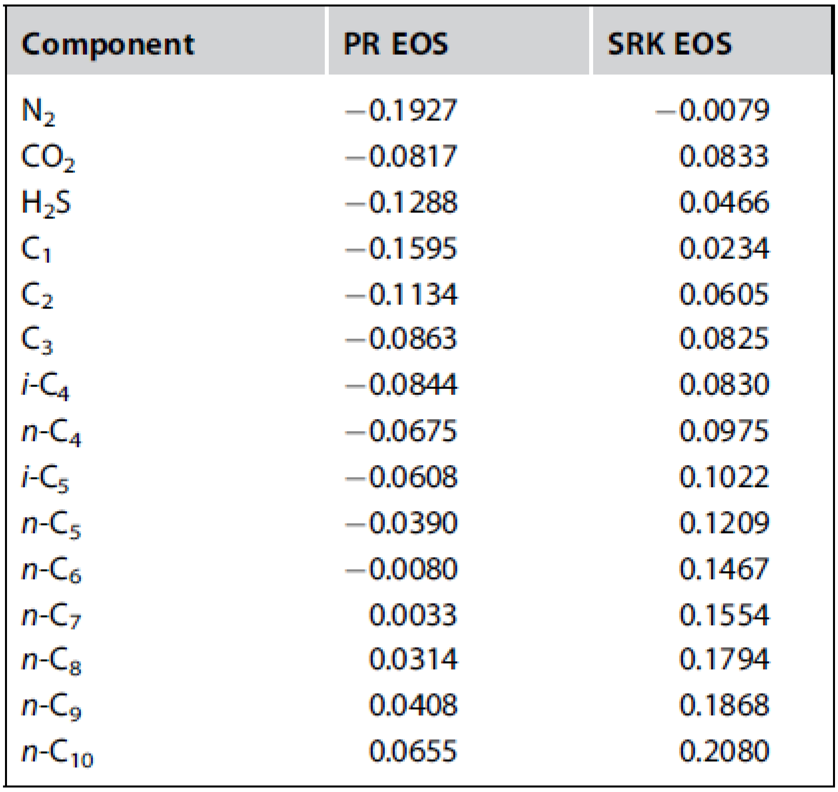
V^V, V^L = volumes of the gas and liquid phases respectively computed by the unmodified PR EOS in m^3/mol

$V^V_{corrected}$, $V^L_{corrected}$ = corrected gas and liquid phase volumes respectively in m^3/mol.

Whitson and Brule (2000) proved that the idea of volume correction could be used for any two constant cubic equations, therefore reducing the volume calculation inaccuracy related to the application of EOS. Whitson and Brule have developed the work of Jhaveri and Youngren (1984) and they put in tables the shift parameter, Si, for some number of pure components. The values in the Table 3, are utilized in Eq. [2.67] to compute the correction factor, ci, for the SRK and PR EOS, see Table 3.

Jhaveri and Youngren (1984) suggested this formula to calculate the shift parameter for C7+ components:

$$S_{c7+} = 1 - \frac{d}{(M)^e} \quad [2.70]$$



Component	PR EOS	SRK EOS
N_2	−0.1927	−0.0079
CO_2	−0.0817	0.0833
H_2S	−0.1288	0.0466
C_1	−0.1595	0.0234
C_2	−0.1134	0.0605
C_3	−0.0863	0.0825
i-C_4	−0.0844	0.0830
n-C_4	−0.0675	0.0975
i-C_5	−0.0608	0.1022
n-C_5	−0.0390	0.1209
n-C_6	−0.0080	0.1467
n-C_7	0.0033	0.1554
n-C_8	0.0314	0.1794
n-C_9	0.0408	0.1868
n-C_{10}	0.0655	0.2080

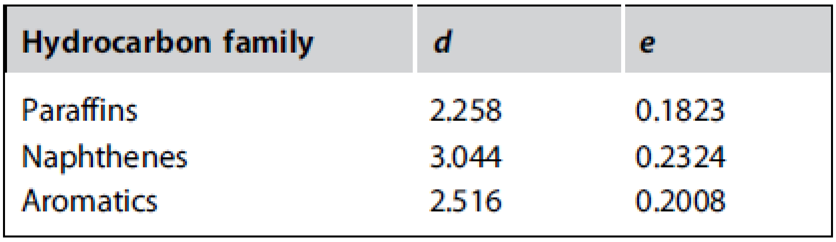
Table 3: Calculation of the volume correction parameter for PR and SRK EOS, (Whitson and Brule, 2000)

where:

M is the molecular weight for the C7+ portion

d, e are the positive correlation coefficients

it was suggested that by Jhaveri and Youngren (1984), if there is no experimental information that needed to calculate (e) and (d), the coefficient (e) could be assumed with value = 0.2051 and the coefficient (d) which is used for matching the C7+ density can be assumed to have values in the range between 2.1 and 3.1. Generally, the values in Table 4 can be used for C7+ portion, for different hydrocarbon families.



Hydrocarbon family	*d*	*e*
Paraffins	2.258	0.1823
Naphthenes	3.044	0.2324
Aromatics	2.516	0.2008

Table 4: Values of d, e suggested by (Jhaveri and Youngren, 1984)

Chapter 3: Equation of State for Water

3.1 Tait equation

Tait equation is an equation of state, which used to correlate density of liquid to pressure. Originally the equation took the name of the publisher Peter Guthrie Tait in 1888 and expressed as:

$$\frac{V_O - V}{(P - P_O)V_O} = -\frac{1}{V_O}\frac{\Delta V}{\Delta P} = \frac{A}{\Pi + (P - P_O)} \quad [3.1]$$

where P_O is reference pressure (1 atmosphere), P is current pressure, V_O is the fresh water volume at reference pressure, V is volume at present pressure, and A, Π are parameters which is calculated experimentally.

In 1895, Tait equation (isothermal) was substituted with Tammann with the following form:

$$-\frac{1}{V_O}\frac{\Delta V}{\Delta P} = \frac{A}{V(P+B)} \quad [3.2]$$

the temperature dependent form of the previous equation is well known as the Tait equation and can be expressed as:

$$\beta = \frac{1}{\mathrm{V}}\left(\frac{\partial v}{\partial p}\right)_T = \frac{0.4343C}{V(P+B)} \quad [3.3]$$

or could be written in integrated form as:

$$V = V_o - C\log\frac{B+P}{B+1} \quad [3.4]$$

where:

β = substance compressibility (often, water) (bar^{-1} or Pa^{-1})

V = substance specific volume (ml/g or m^3/kg)

V_o = specific volume at P= P_o= 1 bar

B and C are temperature functions and independent of pressure.

The formula of the pressure in terms of the specific volume can be expressed as:

$$P = (B + P_o)10^{\left(-\frac{V - V_O}{C}\right)} - B$$

from compressional water data and in a range of temperature from 25° to 85°C, Gibson and Loeffier (1941) found that C in Eq. [3.3] is equal to (0.3150 x V_o), or in other form, $C/V_o = 0.3150$ is temperature independent. Furthermore, B could be represented as:

$$B = 2996 + 7.5554(T - 25) - 0.17814(T - 25)^2 + 608\,x10^{-6}(T - 25)^3 \quad [3.5]$$

Gibson (1935) developed Tait equation as he introduced additional parameter which is called effective pressure, Pe, and by assuming that the volume of 1 gram of solution containing X_1 grams of solvent and X_2 grams of solute could be represented as:

$$V = X_1\psi_1 + X_2\psi_2 \quad [3.6]$$

where:

ψ_1= apparent specific volume for solvent in the solution (ml/g).

ψ_2 = apparent specific volume of the solute.

X_1 and X_2 = weight fraction of solvent and solute, respectively.

Then, the PV relationship for solution could be expressed by Harned and Owen (1958) as:

$$V * \beta = -\left(\frac{\partial v}{\partial p}\right)_T = \frac{0.4343X_1C}{B+P_e+P} - X_2\frac{\partial\psi_2}{\partial p} \quad [3.7]$$

$$V * \beta \approx \frac{0.4343X_1C}{B^*+P} \quad [3.8]$$

or in integrated form:

$$V = V_o - X_1C\log\frac{B+P_e+P}{B+P_e+1} - X_2(\psi_2 - \psi_{2O}) \quad [3.9]$$

$$V \approx V_o - X_1C\log\frac{B^*+P}{B^*+1} \quad [3.10]$$

where $B^* = B + P_e$, since at moderate pressure and concentration $(\psi_2 - \psi_{2O})$ and X_2 are both small, the last terms in Eqs. [3.7] and [3.9] are negligible.

So, many calculations aimed to discover B for water and B* for sea water with application of Eqs. [3.3], [3.4], [3.8] and [3.10] to different sources of data. Gibson's $C/V_o = 0.3150$ was used basically to compare between different data.

Note that all pressure units were converted into bars before any computations.

3.2 B calculations for Pure Water

From PVT data of Amagat (1893) & Newton and Kennedy (1965) & Kennedy et al (1958), and by rearranging Eq. [3.4]:

$$B = \frac{P-1}{exp^{\left[\frac{1-V/V_O}{0.1368}\right]}-1} - 1 \quad [3.11]$$

B is calculated at different pressure and should be independent of pressure, when the equation of Tait (1888) is valid. The results, as shown in Tables 5, 6, 7 and 8 and summarized in Figure 10, it could be concluded that, except for B's at pressures lower than 300 bars that will have a higher scattering. In averaging B, values between 400 and 1000 bars only should be considered.

For the values of B between 400 and 1000 bars, Amagat's Table 5 indicates uniformly small errors (less than 0.1%) up to temperature= 60ºC. While for temperatures higher than 60ºC, as temperature increases the error for B values increases.

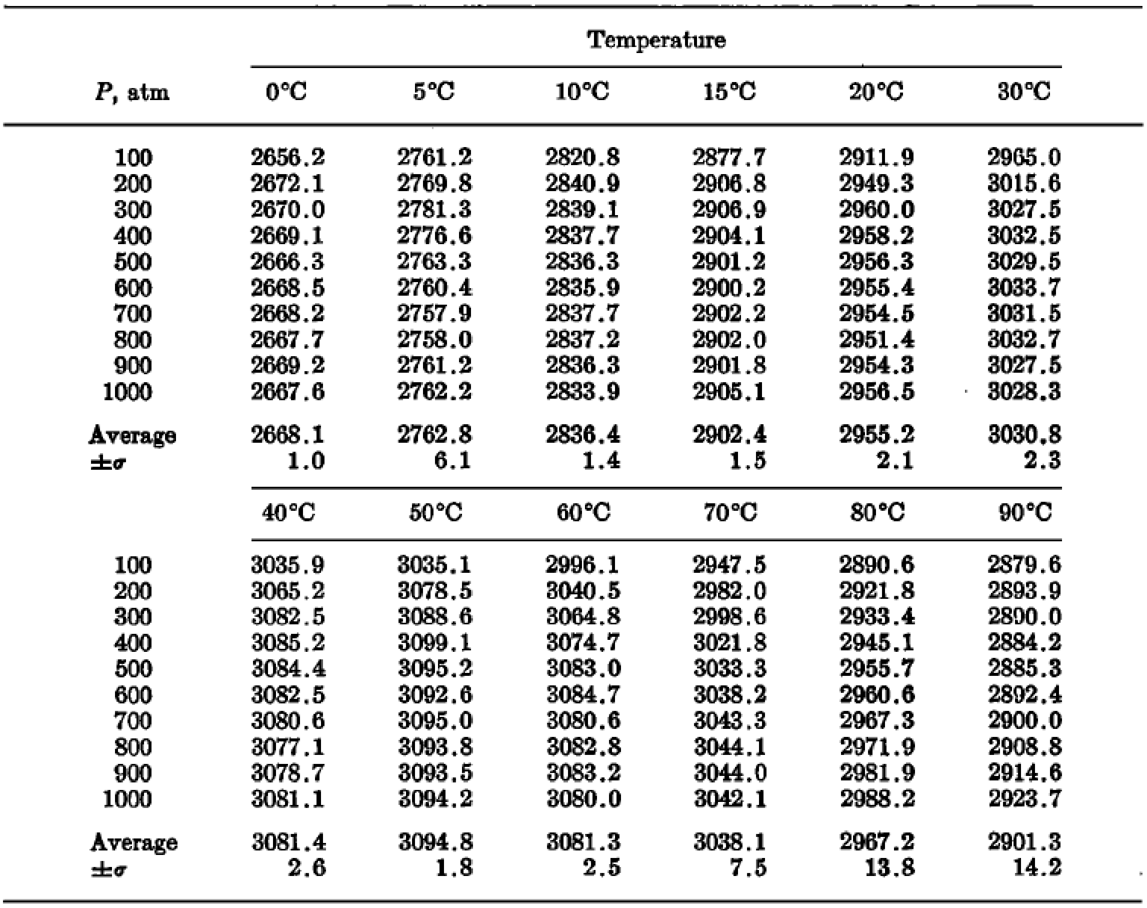
Amagat's Table 6 shows greater error of B (about 0.3%) excepting T= 0ºC, but B values still following closely the data in the previous table. Moreover, B at pressure greater than 1500 bars is highly arbitrary.

Values of B at 0ºC as in Table 8 of Newton and Kennedy (1965) have good agreement with the values of Amagat (Dorsey, 1940). The other values of B of Kennedy et al. (1958), (Tables 7 and 8) are systematically lower than Amagat’s values, so they have agreement. The percentage of error for B values in Table 7 is only lower than 0.3%, while in Table 8, is about 0.2%.

From Ekman's apparent bulk compression data (1908). The bulk compression K_o, by definition equal to $1 - V/Vo$, of water was obtained from apparent compression K_o' data through an expression as in the following relation:

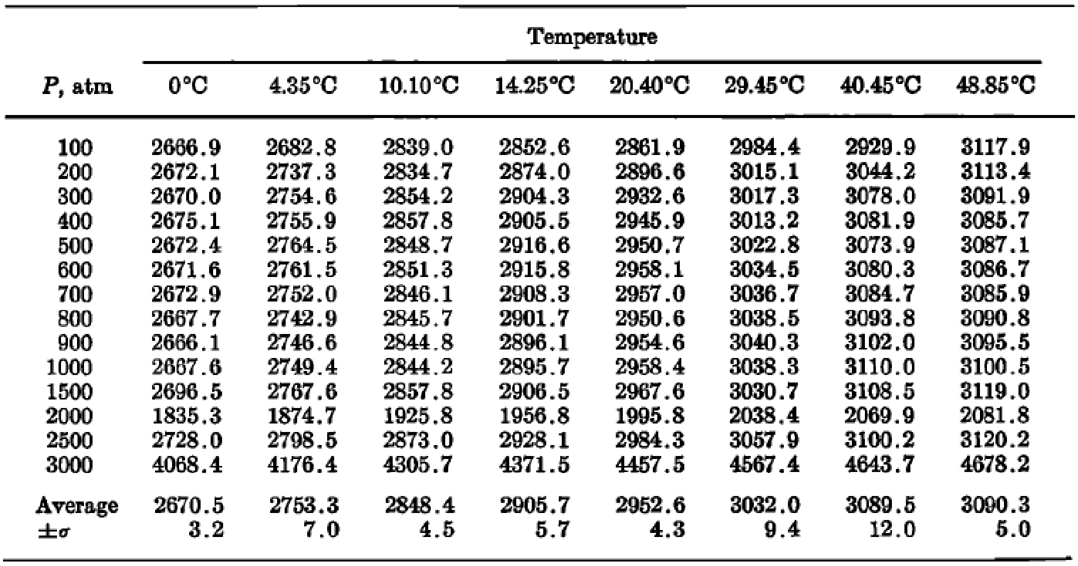
$$K_o = K_o'\left(1 - K_g\right) + K_g \quad [3.12]$$

where Kg, is the glass compression that contain the water. $Kg = (P-1)v$, where the average compressibility of glass $v = 0\,.225X10^{-5}\ bar^{-1}$ was used in the calculations. And by Eq. [3.11], B values have been determined as shown in Table 9. The table indicates that Ekman's data are true and consistent. The standard deviation of B is lower than 0.03%, values of B are slightly higher than the value in Amagat's Table 5. Since both Amagat's and Ekman's zero degree temperature data have good agreement with that of Tait equation. Then Ekman (1908) suggested revised value for average compressibility of glass $v = 0\ .215X10^{-5}bar^{-1}$ but this revised value tend to increase the values of B only 1 bar, which still uncertain experimentally.



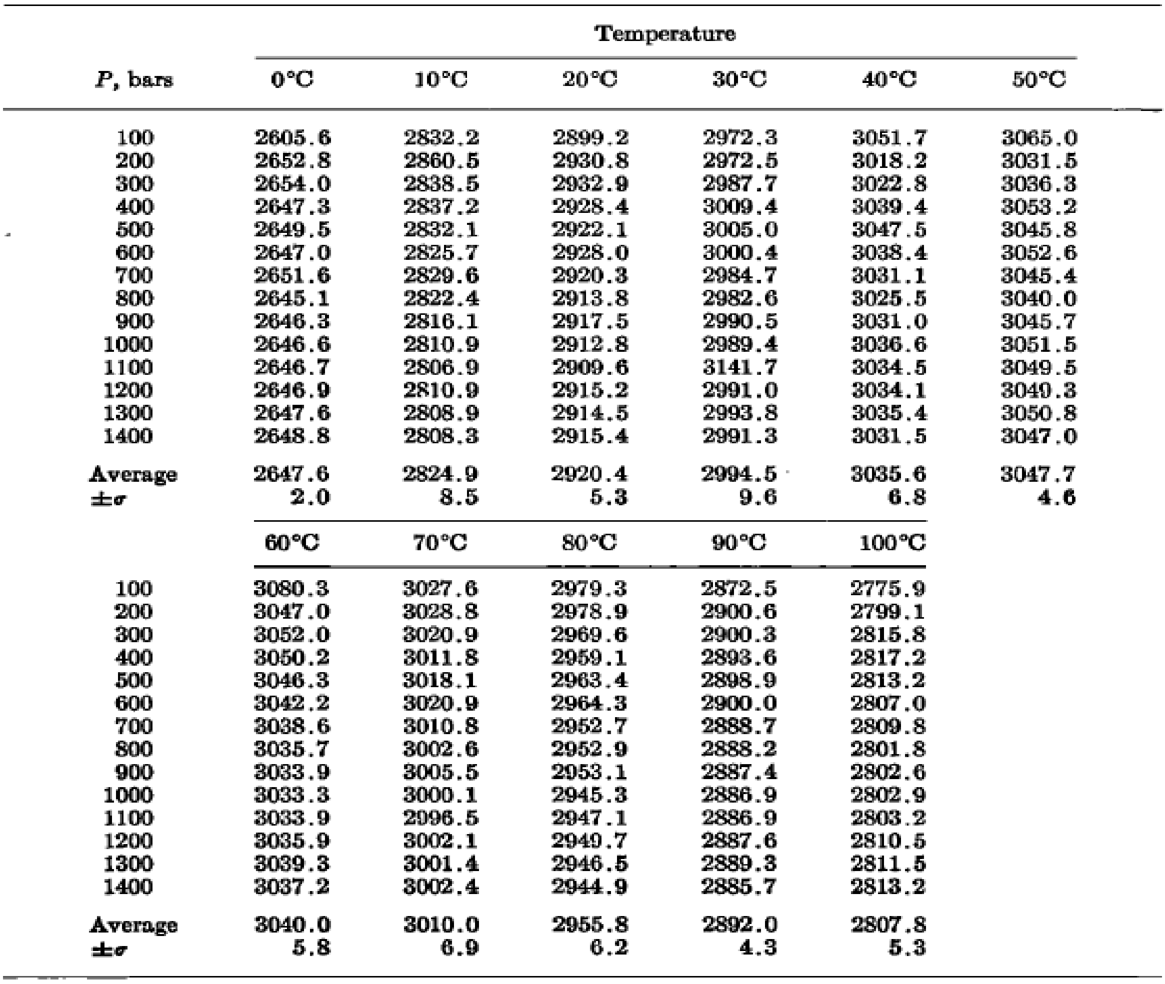
	Temperature					
P, atm	0°C	5°C	10°C	15°C	20°C	30°C
100	2656.2	2761.2	2820.8	2877.7	2911.9	2965.0
200	2672.1	2769.8	2840.9	2906.8	2949.3	3015.6
300	2670.0	2781.3	2839.1	2906.9	2960.0	3027.5
400	2669.1	2776.6	2837.7	2904.1	2958.2	3032.5
500	2666.3	2763.3	2836.3	2901.2	2956.3	3029.5
600	2668.5	2760.4	2835.9	2900.2	2955.4	3033.7
700	2668.2	2757.9	2837.7	2902.2	2954.5	3031.5
800	2667.7	2758.0	2837.2	2902.0	2951.4	3032.7
900	2669.2	2761.2	2836.3	2901.8	2954.3	3027.5
1000	2667.6	2762.2	2833.9	2905.1	2956.5	3028.3
Average	2668.1	2762.8	2836.4	2902.4	2955.2	3030.8
±σ	1.0	6.1	1.4	1.5	2.1	2.3
	40°C	50°C	60°C	70°C	80°C	90°C
100	3035.9	3035.1	2996.1	2947.5	2890.6	2879.6
200	3065.2	3078.5	3040.5	2982.0	2921.8	2893.9
300	3082.5	3088.6	3064.8	2998.6	2933.4	2800.0
400	3085.2	3099.1	3074.7	3021.8	2945.1	2884.2
500	3084.4	3095.2	3083.0	3033.3	2955.7	2885.3
600	3082.5	3092.6	3084.7	3038.2	2960.6	2892.4
700	3080.6	3095.0	3080.6	3043.3	2967.3	2900.0
800	3077.1	3093.8	3082.8	3044.1	2971.9	2908.8
900	3078.7	3093.5	3083.2	3044.0	2981.9	2914.6
1000	3081.1	3094.2	3080.0	3042.1	2988.2	2923.7
Average	3081.4	3094.8	3081.3	3038.1	2967.2	2901.3
±σ	2.6	1.8	2.5	7.5	13.8	14.2

Table 5: B of Water Calculated from Data of Amagat (1893) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967).



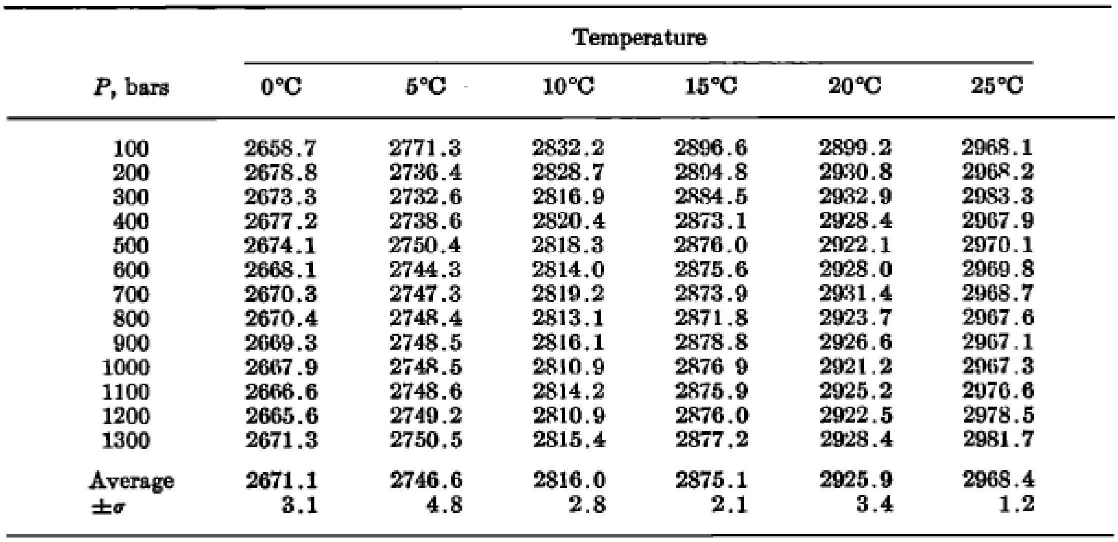
P, atm	Temperature 0°C	4.35°C	10.10°C	14.25°C	20.40°C	29.45°C	40.45°C	48.85°C
100	2666.9	2682.8	2839.0	2852.6	2861.9	2984.4	2929.9	3117.9
200	2672.1	2737.3	2834.7	2874.0	2896.6	3015.1	3044.2	3113.4
300	2670.0	2754.6	2854.2	2904.3	2932.6	3017.3	3078.0	3091.9
400	2675.1	2755.9	2857.8	2905.5	2945.9	3013.2	3081.9	3085.7
500	2672.4	2764.5	2848.7	2916.6	2950.7	3022.8	3073.9	3087.1
600	2671.6	2761.5	2851.3	2915.8	2958.1	3034.5	3080.3	3086.7
700	2672.9	2752.0	2846.1	2908.3	2957.0	3036.7	3084.7	3085.9
800	2667.7	2742.9	2845.7	2901.7	2950.6	3038.5	3093.8	3090.8
900	2666.1	2746.6	2844.8	2896.1	2954.6	3040.3	3102.0	3095.5
1000	2667.6	2749.4	2844.2	2895.7	2958.4	3038.3	3110.0	3100.5
1500	2696.5	2767.6	2857.8	2906.5	2967.6	3030.7	3108.5	3119.0
2000	1835.3	1874.7	1925.8	1956.8	1995.8	2038.4	2069.9	2081.8
2500	2728.0	2798.5	2873.0	2928.1	2984.3	3057.9	3100.2	3120.2
3000	4068.4	4176.4	4305.7	4371.5	4457.5	4567.4	4643.7	4678.2
Average	2670.5	2753.3	2848.4	2905.7	2952.6	3032.0	3089.5	3090.3
±σ	3.2	7.0	4.5	5.7	4.3	9.4	12.0	5.0

Table 6: B of Water Calculated from Data of Amagat (1893) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967).



P, bars	Temperature 0°C	10°C	20°C	30°C	40°C	50°C
100	2605.6	2832.2	2899.2	2972.3	3051.7	3065.0
200	2652.8	2860.5	2930.8	2972.5	3018.2	3031.5
300	2654.0	2838.5	2932.9	2987.7	3022.8	3036.3
400	2647.3	2837.2	2928.4	3009.4	3039.4	3053.2
500	2649.5	2832.1	2922.1	3005.0	3047.5	3045.8
600	2647.0	2825.7	2928.0	3000.4	3038.4	3052.6
700	2651.6	2829.6	2920.3	2984.7	3031.1	3045.4
800	2645.1	2822.4	2913.8	2982.6	3025.5	3040.0
900	2646.3	2816.1	2917.5	2990.5	3031.0	3045.7
1000	2646.6	2810.9	2912.8	2989.4	3036.6	3051.5
1100	2646.7	2806.9	2909.6	3141.7	3034.5	3049.5
1200	2646.9	2810.9	2915.2	2991.0	3034.1	3040.3
1300	2647.6	2808.9	2914.5	2993.8	3035.4	3050.8
1400	2648.8	2808.3	2915.4	2991.3	3031.5	3047.0
Average	2647.6	2824.9	2920.4	2994.5	3035.6	3047.7
±σ	2.0	8.5	5.3	9.6	6.8	4.6
	60°C	70°C	80°C	90°C	100°C	
100	3080.3	3027.6	2979.3	2872.5	2775.9	
200	3047.0	3028.8	2978.9	2900.6	2799.1	
300	3052.0	3020.9	2969.6	2900.3	2815.8	
400	3050.2	3011.8	2959.1	2893.6	2817.2	
500	3046.3	3018.1	2963.4	2898.9	2813.2	
600	3042.2	3020.9	2964.3	2900.0	2807.0	
700	3038.6	3010.8	2952.7	2888.7	2809.8	
800	3035.7	3002.6	2952.9	2888.2	2801.8	
900	3033.9	3005.5	2953.1	2887.4	2802.6	
1000	3033.3	3000.1	2945.3	2886.9	2802.9	
1100	3033.9	2996.5	2947.1	2886.9	2803.2	
1200	3035.9	3002.1	2949.7	2887.6	2810.5	
1300	3039.3	3001.4	2946.5	2889.3	2811.5	
1400	3037.2	3002.4	2944.9	2885.7	2813.2	
Average	3040.0	3010.0	2955.8	2892.0	2807.8	
±σ	5.8	6.9	6.2	4.3	5.3	

Table 7: B of Water Calculated from Data of Kennedy (1958) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967).



P, bars	Temperature 0°C	5°C	10°C	15°C	20°C	25°C
100	2658.7	2771.3	2832.2	2896.6	2899.2	2968.1
200	2678.8	2736.4	2828.7	2804.8	2930.8	2968.2
300	2673.3	2732.6	2816.9	2884.5	2932.9	2983.3
400	2677.2	2738.6	2820.4	2873.1	2928.4	2967.9
500	2674.1	2750.4	2818.3	2876.0	2922.1	2970.1
600	2668.1	2744.3	2814.0	2875.6	2928.0	2969.8
700	2670.3	2747.3	2819.2	2873.9	2931.4	2968.7
800	2670.4	2748.4	2813.1	2871.8	2923.7	2967.6
900	2669.3	2748.5	2816.1	2878.8	2926.6	2967.1
1000	2667.9	2748.5	2810.9	2876 9	2921.2	2967.3
1100	2666.6	2748.6	2814.2	2875.9	2925.2	2970.6
1200	2665.6	2749.2	2810.9	2876.0	2922.5	2978.5
1300	2671.3	2750.5	2815.4	2877.2	2928.4	2981.7
Average	2671.1	2746.6	2816.0	2875.1	2925.9	2968.4
$\pm\sigma$	3.1	4.8	2.8	2.1	3.4	1.2

Table 8: B of Water determined from Newton and Kennedy Data (1965) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967).

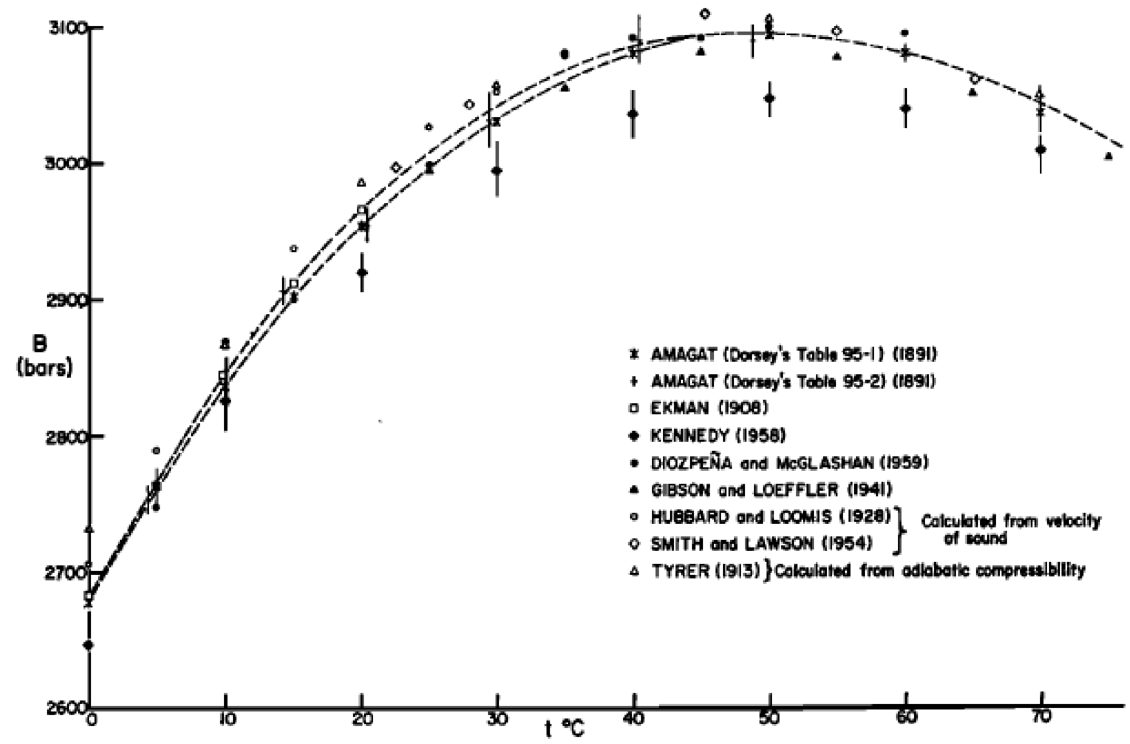
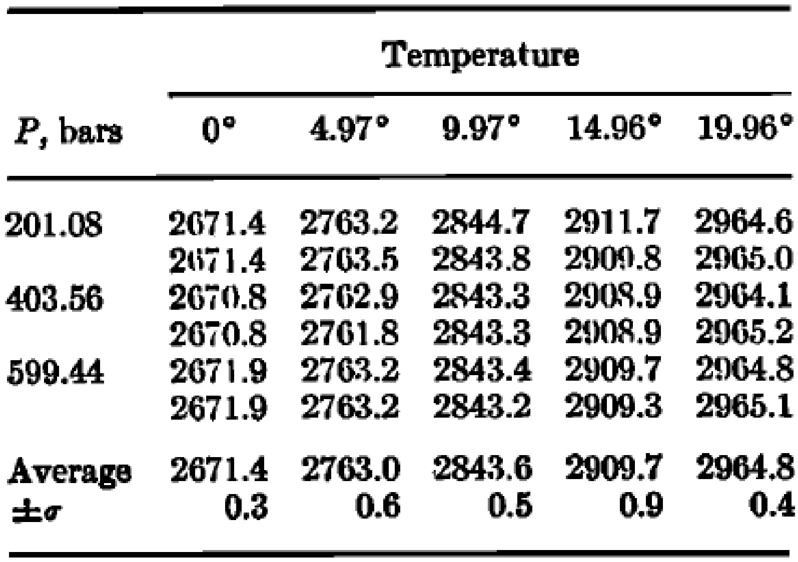


Figure 10: B of water as a function of temperature, (Yuan-Hui Li, 1967).



	Temperature				
P, bars	0°	4.97°	9.97°	14.96°	19.96°
201.08	2671.4	2763.2	2844.7	2911.7	2964.6
	2671.4	2763.5	2843.8	2909.8	2965.0
403.56	2670.8	2762.9	2843.3	2908.9	2964.1
	2670.8	2761.8	2843.3	2908.9	2965.2
599.44	2671.9	2763.2	2843.4	2909.7	2964.8
	2671.9	2763.2	2843.2	2909.3	2965.1
Average	2671.4	2763.0	2843.6	2909.7	2964.8
$\pm\sigma$	0.3	0.6	0.5	0.9	0.4

Table 9: B of Water determined from Ekman Data (1908) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967).

From compressibility data of Diaz Pena and McGlashan (1959), the water isothermal compressibility at pressure = 1 atm β_o was calculated from data which are associated to water compression at temperatures up to 60°C and Pressures up to 30 atm.

By arranging Eq. [3.3], it could be obtained:

$$B = 0.1368/\beta_o - 1 \quad [3.13]$$

B values were computed and the results which are given in Table 10 and Figure 10, have very good agreement with Amagat's Table 5 despite of the very wide pressure range. Note that the value of B is pressure independent.

From the sound velocity data in water by Wilson (1960), the water isothermal compressibility β_o at atmospheric pressure was computed through the following relations:

$$\beta_s = 10^6 x\, V/\mu^2 \quad [3.14]$$

$$\beta = \beta_s + 0.1T\alpha^2\, V/C_p \quad [3.15]$$

where:

V= specific volume (cm^3/g).

μ = sound velocity (cm/sec).

Cp = specific heat (joules/deg.gram).

T = absolute temperature (K).

β = isothermal compressibility (bar^{-1}).

β_s = adiabatic compressibility (bar^{-1}).

$$\alpha = \frac{1}{V}\frac{\partial V}{\partial T} = -\frac{1}{\rho}\frac{\partial \rho}{\partial T} \quad [3.16]$$

the atmospheric data of μ are taken from Wilson (1959), α and V are computed by Chappins' equation (Dorsey, 1940), and C_p is taken from Cox and Smith (1959). After this, by using Eq. [3.13], B was determined.

B for Wilson can be represented by the equation:

$$B = 2689.81 + 20.223T - 0.3081T^2 + 1.38\,x10^{-3}T^3 \quad [3.17]$$

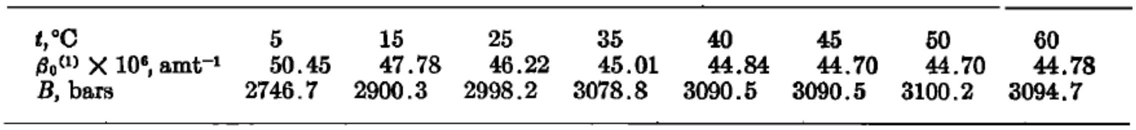
where β_o is calculated from measurements of adiabatic compressibility and the sound velocity in water.

Once B values are known, V, α and β at pressure P could be computed by the Tait (1888) equation, and the velocity of sound at greater pressures can be calculated by Eqs. [3.14] and [3.15].

There is difference of B values determined by Ekman's data and by using Wilson's atmospheric sound velocity through water, two reasons may explain this:

1. The quantity B could be pressure dependent at lower pressure, but this explanation can hardly be reconciled with the results of Diaz Pena and McGlashan (1959).
2. As Crease (1962) noticed, since sound velocity measurements have been made with high frequency pulses, it is possible that the water does not remain in equilibrium at lower pressure, so Del Grosso (1952) has found that this effect is probably going to be little.

In summary, it is noticed that the most consistent PVT data for water are the values of Amagat (1893) and values of Ekman (1908), which are more than 50 years old.



t, °C	5	15	25	35	40	45	50	60
$\beta_0^{(1)} \times 10^6$, amt^{-1}	50.45	47.78	46.22	45.01	44.84	44.70	44.70	44.78
B, bars	2746.7	2900.3	2998.2	3078.8	3090.5	3090.5	3100.2	3094.7

Table 10: B of Water determined from Diaz pena and McGlashan Data (1959) in Units of Bars and C/Vo=0.3150, (Yuan-Hui Li, 1967).

B values of Amagat's (1893) Table 5 can be represented as:

$$B = 2688 + 10.867T - 0.3111T^2 + 1.778\,x10^{-3}T^3 \text{ [3.18]}$$

in the range between 0° and 45°C.

$$B = 3009.4 + 7.555(T-25) - 0.1781(T-25)^2 + 0.608\,x10^{-3}(T-25)^3 \text{ [3.19]}$$

for T > 45°C.

For B values of Ekman (1908):

$$B = 2670.8 + 19.9T - 0.26T^2 \text{ [3.20]}$$

in the range 0° and 20°C.

For B values of Newton and Kennedy (1965):

$$B = 2627.9 + 15.97T - 0.166T^2 \text{ [3.21]}$$

for 0°C< T < 25°C.

$$B = 2968.4 + 7.555(T-25) - 0.1781(T-25)^2 + 0.608\,x10^{-3}(T-25)^3 \text{ [3.22]}$$

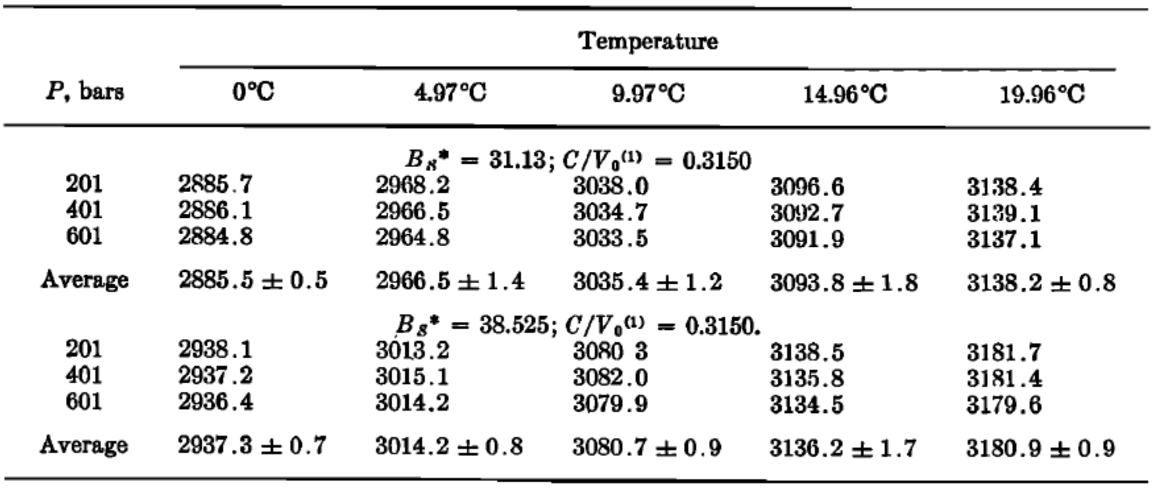
for T > 25°C.

The curvatures of B, which is function in temperature, by both Wilson and Ekman are consistent between each other. For high temperatures (T > 30°C), the curvatures of B by Amagat and Kennedy et al. have good agreement with that by Gibson and Loeffier, as shown in Figure 10.

3.3 B* calculations for Sea Water

The PVT data for sea water are initially based on Ekman's (1908) compression Calculations for two different salinity sea waters and Knudsen's (1901) PVT data for sea water with different chlorinity at atmospheric pressure. The summarized data of Ekman's and Knudsen's are given in Dorsey's Table 109-A and Table 108, respectively (Dorsey, 1940, p. 248).

Applying Dorsey's Table 109-A to Eq. [3.10], B* values were calculated as given in Table 11 and Figure 11. Note that B* is independent of pressure.



	Temperature				
P, bars	0°C	4.97°C	9.97°C	14.96°C	19.96°C
		$B_S{}^* = 31.13$; $C/V_0{}^{(1)} = 0.3150$			
201	2885.7	2968.2	3038.0	3096.6	3138.4
401	2886.1	2966.5	3034.7	3092.7	3139.1
601	2884.8	2964.8	3033.5	3091.9	3137.1
Average	2885.5 ± 0.5	2966.5 ± 1.4	3035.4 ± 1.2	3093.8 ± 1.8	3138.2 ± 0.8
		$B_S{}^* = 38.525$; $C/V_0{}^{(1)} = 0.3150.$			
201	2938.1	3013.2	3080.3	3138.5	3181.7
401	2937.2	3015.1	3082.0	3135.8	3181.4
601	2936.4	3014.2	3079.9	3134.5	3179.6
Average	2937.3 ± 0.7	3014.2 ± 0.8	3080.7 ± 0.9	3136.2 ± 1.7	3180.9 ± 0.9

Table 11: B* of sea Water detrmined from Ekman's Data (1908), (Yuan-Hui Li, 1967).

B* could be represented as a parabolic function of temperature by:

$$B^*_{@S=38.525} = 2936.5 + 16.68T - 0.223T^2 \quad [3.23]$$

$$B^*_{@S=31.13} = 2885.5 + 17.2T - 0.223T^2 \quad [3.24]$$

for a range of temperature from 0° to 20°C.

For most electrolysis solutions with one salt with concentration lower than 1 molarity B* is a linear function of molarity, Gibson (1935), Eqs. [3.23] and [3.24] could be linearly extrapolated back to zero salinity:

$$B^*_{@S=0} = B = 2670.8 + 19.39T - 0.223T^2 \quad [3.25]$$

the good agreement between Eq. [3.25] and B values calculated from Ekman's compression data on water, as indicated in Figure 12, shows excellent consistency of compression calculations by Ekman for both sea water and fresh water.

As a summary the PVT relationship for sea water with temperature range of 0°C < T< 20°C, 30% < S < 40% and 1 < P < 1000 bars, can be expressed as:

$$V = V_o - (1 - Sx10^{-3})x\, C \log\frac{B^*+P}{B^*+1} \quad [3.26]$$

where C = 0.3150xV$_o$ and S is salinity % and where:

$$B^* = (2670.8 + 6.8966S) + (19.3 - 0.0703S)T - 0.223T^2 \quad [3.27]$$

to assure the validity of Eq. [3.26] the specific volume of sea water at 0°C and with salinity 35% and at different pressures have been computed by Eq. [3.26] and are compared with values of V, V$_o$ found in Bjerknes and sandstrom's (1910) table, which were based on Ekman's data by applying his sea water equation of state . The results show excellent agreement between them.

To check on the validity of the Tait-Gibson equation for sea water, the apparent specific volume for water in sea water solution, ψ_1, could be determined through Eq. [3.4] and it could be assumed that ψ_1 is equal to the specific volume of pure water at the pressure applied equal to the effective pressure Pe of the considered solution:

$$\psi_{1o} = V = V_o(1 - 0.315 \log \frac{B^*}{B+1}) \quad [3.28]$$

where B* and B could be determined from Eq. [3.27] for any salinity at different temperatures.

Once ψ_1 is known, ψ_2 can be determined from equation as:

$$\psi_{2o} = (\mathrm{V} - X_1\psi_{1o})/X_2 \quad [3.29]$$

following above procedures ψ_1, ψ_2 for sea water with 38.525% and 31.13% salinity have been determined. The results, as given in Table 12, show that ψ_2 are almost independent of salinity and may be represented as:

$$\psi_{2o} = 0.541 - 0.00219T \quad [3.30]$$

when the temperature and sea water salinity are known, the sea water specific volume under atmospheric pressure can be calculated from:

$$V_o = X_1\psi_{1o} + X_2\psi_{2o} \quad [3.31]$$

Data of Newton and Kennedy (1965) PVTS data on sea water, the B* values for 3 different salinities were determined by Eq. [3.10] B* values for salinities 44.03% and 34.99% in the temperature range between 0°C and 10°C have good agreement with Ekman's values, while all other B* points are very low with respect to values of Ekman. For sea water sound velocity data by Del Grosso (1952) and Wilson (1960). The isothermal compressibilities at atmospheric pressure were calculated from Eqs. [3.14] and [3.15]; then from Eq. [3.8] B* was calculated. The results are plotted in Figure 11.

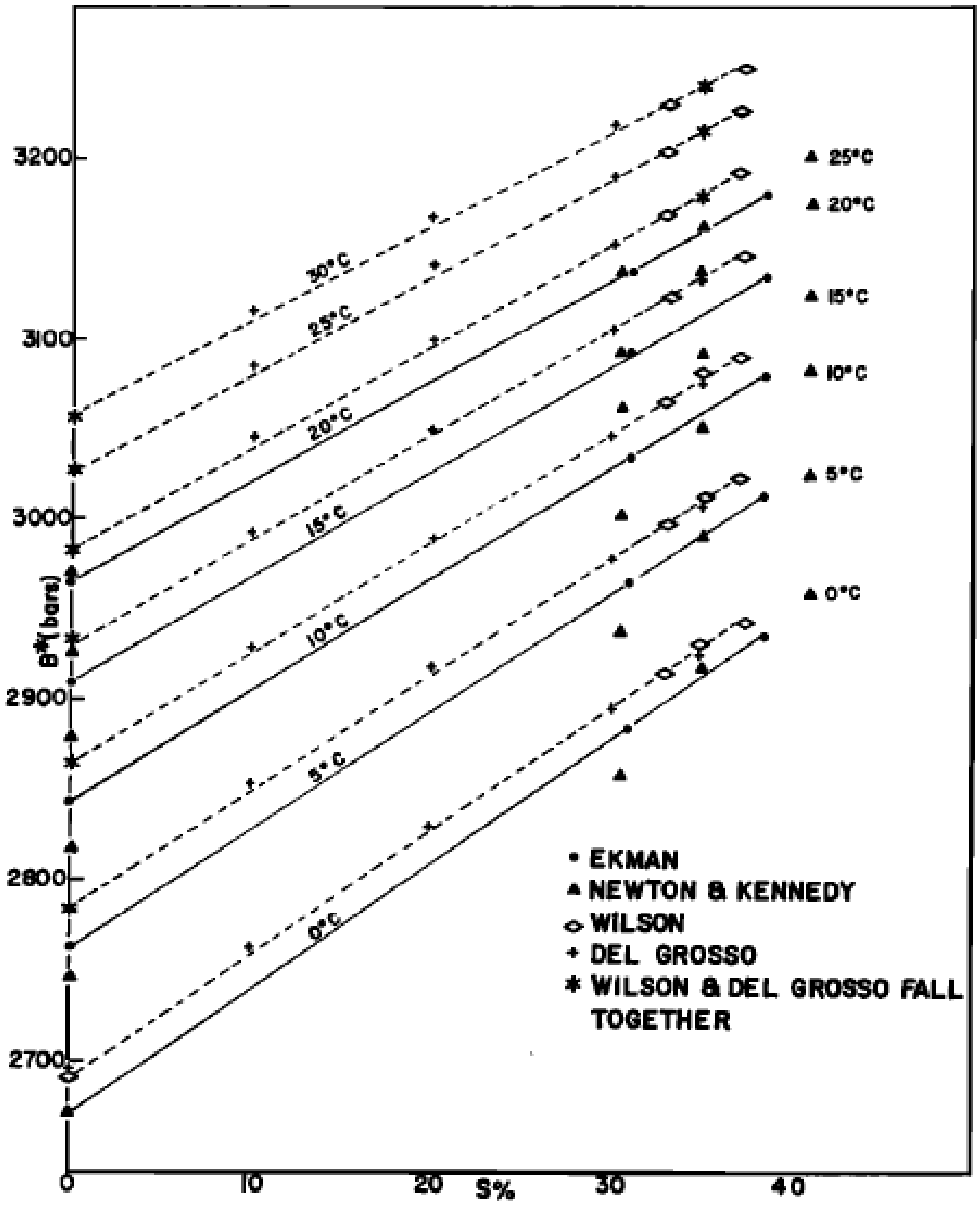


Figure 11: B as a function of salinity, (Yuan-Hui Li, 1967).*

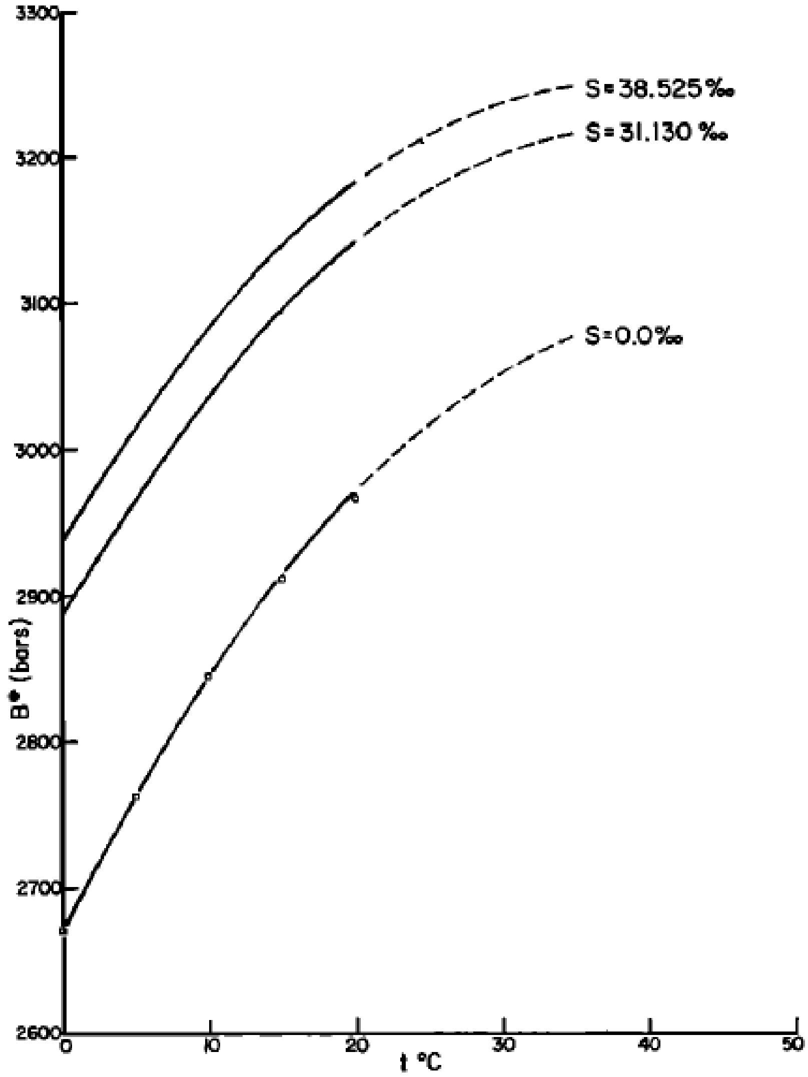
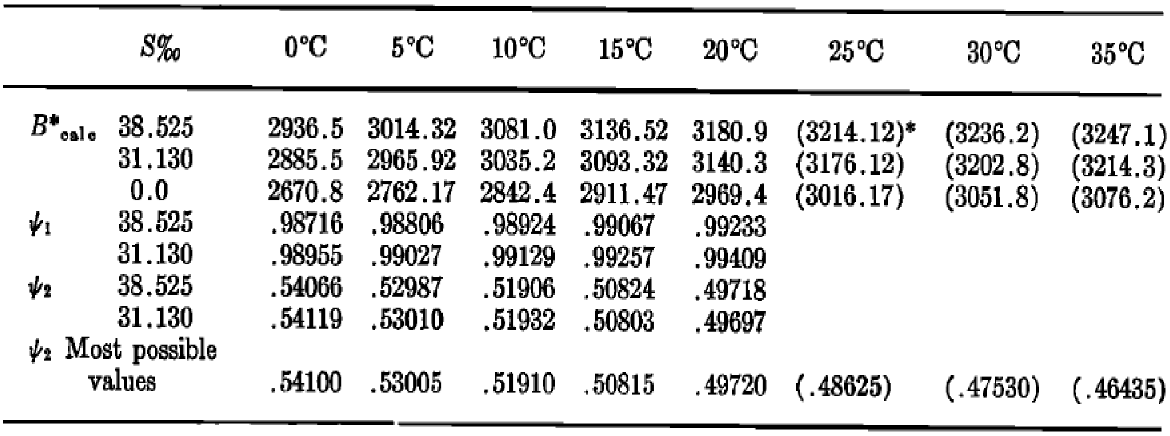


Figure 12: B as a function of salinity and temperature, (Yuan-Hui Li, 1967).*



	S‰	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C
B^*_{calc}	38.525	2936.5	3014.32	3081.0	3136.52	3180.9	(3214.12)*	(3236.2)	(3247.1)
	31.130	2885.5	2965.92	3035.2	3093.32	3140.3	(3176.12)	(3202.8)	(3214.3)
	0.0	2670.8	2762.17	2842.4	2911.47	2969.4	(3016.17)	(3051.8)	(3076.2)
ψ_1	38.525	.98716	.98806	.98924	.99067	.99233			
	31.130	.98955	.99027	.99129	.99257	.99409			
ψ_2	38.525	.54066	.52987	.51906	.50824	.49718			
	31.130	.54119	.53010	.51932	.50803	.49697			
ψ_2 Most possible values		.54100	.53005	.51910	.50815	.49720	(.48625)	(.47530)	(.46435)

Table 12: B, ψ_1 and ψ_2 for Sea Water, (Yuan-Hui Li, 1967).*

Wilson's B* values could be expressed as:

$$B^* = B + S/37(252.59 - 2.883T + 4.365x10^{-2}T^2 - 0.4017x10^{-3}T^3) \quad [3.32]$$

where S = salinity (%) and B is from Eq. [3.17]. Values of B* are greater than values Ekman's (1908) by around 20 bars. The B* values show a linear relationship with salinity, which have the same slopes as values of Ekman.

Note that the disagreements of B*values between Ekman and Wilson could be explained by the same argument used for pure water.

3.4 Murnaghan equation of state

The Murnaghan (1944) model which is sometimes expressed as:

$$\frac{V}{V_o} = [1 + \frac{n}{K_o}(P - P_o)]^{-1/n} \quad [3.33]$$

where:

V_o = the specific volume at pressure P_o

V = the specific volume at pressure P

K_o = the bulk modulus at P_o

n = material parameter

the equation, in pressure form, could be written as:

$$P = \frac{K_o}{n}\left[\left(\frac{V_o}{V}\right)^n - 1\right] + P_o = \frac{K_o}{n}\left[\left(\frac{\rho}{\rho_o}\right)^n - 1\right] + P_o \quad [3.34]$$

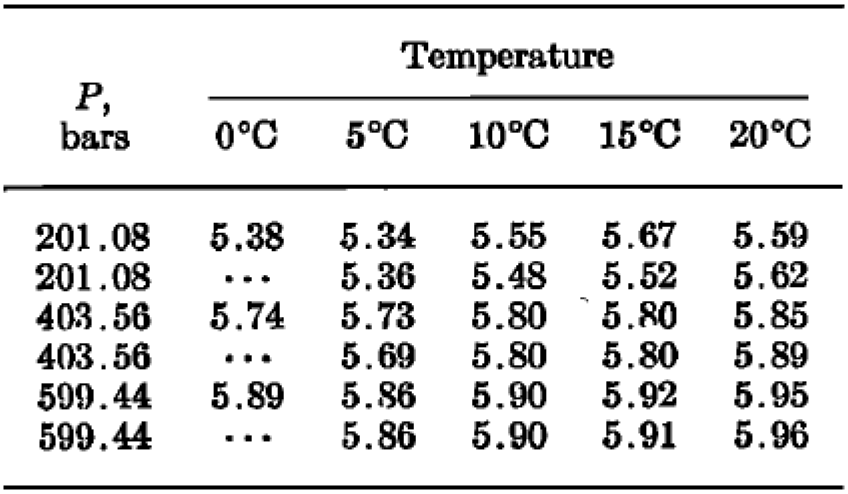
where:

ρ, ρ_o are mass densities at P, Po, respectively.

The (n) parameter in equation of Murnaghan was calculated for Ekman's water data. The results are given in Tables 13, 14 and can be represented as:

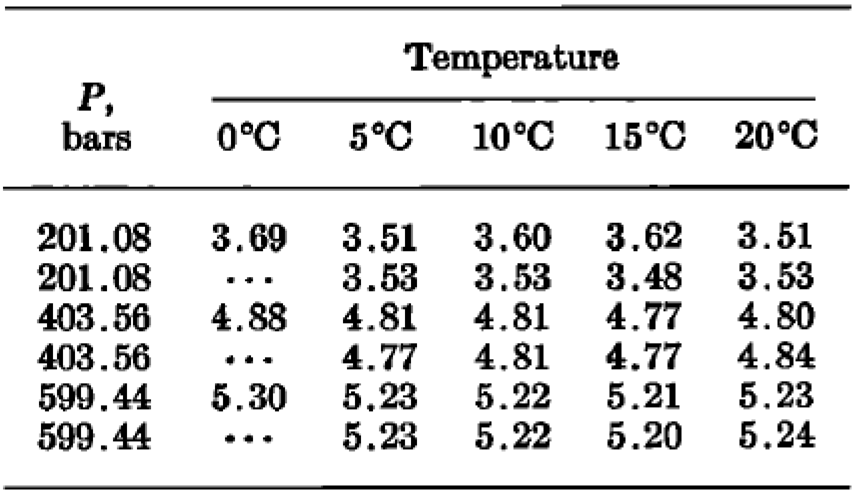
$$n = \frac{1}{(P-1)\beta_o}\left[\left(\frac{V_o}{V}\right)^n - 1\right] \quad [3.35]$$

the compressibility of water at atmospheric pressure, β_o, have been taken from sound velocity data and from the data of Diaz Pena and McGlashan (1959).



P, bars	Temperature				
	0°C	5°C	10°C	15°C	20°C
201.08	5.38	5.34	5.55	5.67	5.59
201.08	···	5.36	5.48	5.52	5.62
403.56	5.74	5.73	5.80	5.80	5.85
403.56	···	5.69	5.80	5.80	5.89
599.44	5.89	5.86	5.90	5.92	5.95
599.44	···	5.86	5.90	5.91	5.96

Table 13: n Value of Murnaghan Equation for Ekman's PVT Data of Water β_0 from M. Diaz Pena and M. L. McGlashan (1959), (Yuan-Hui Li, 1967).



P, bars	Temperature				
	0°C	5°C	10°C	15°C	20°C
201.08	3.69	3.51	3.60	3.62	3.51
201.08	···	3.53	3.53	3.48	3.53
403.56	4.88	4.81	4.81	4.77	4.80
403.56	···	4.77	4.81	4.77	4.84
599.44	5.30	5.23	5.22	5.21	5.23
599.44	···	5.23	5.22	5.20	5.24

Table 14: n Value of Murnaghan Equation for Ekman's PVT Data (1908) of Water β_0 from sound velocity data, (Yuan-Hui Li, 1967).

Chapter 4: Conclusion

Ideal gas equation has a lot of limitations regarding it’s applicability at real reservoir conditions and for wide range of temperatures and pressures, this have led to many trials to develop equation of state more suitable and accurate for description of the behavior of real reservoir fluids.

As van der Waals (1873) introduced his equation of state, it used to generalize the ideal gas law based on the fact that gases behave as real gases, even it doesn’t have any practical applications nowadays it was considered the basis for revolution in developing and enhancing EOS.

In Redlich and Kwong equation they included the temperature of the system to the van der Waals attraction term to consider its effects on the intermolecular attractive forces among the atoms which has improved the equation accuracy. Anyway, RK EOS were not the last possible improvements to the VdW equation of state, the Soave-RK EOS was born as modification on RK EOS with a very good potential.

SRK equation had overcome the fact that the RK equation was not accurate to express the effect of temperature which in turn improved the application of the equation of state to multicomponent vapor-liquid equilibrium (VLE) calculations.

Then, Peng and Robinson improved the ability of the equation of state for prediction of densities of liquid and other fluid properties, particularly near the critical zone.

Finally, Peneloux et al. (1982) introduced a way to improve the volume predictions for the two parameter SRK EOS by using a volume correction factor, similarly Jhaveri and Youngren (1984) used volume correction factor for the two parameter PR EOS.

Furthermore, for water and by using Tait equation of state the results could be summarized in the following points:

- The most internally consistent PVT data on water compared to the Tait equation are the values of Ekman and of Amagat.
- Ekman's compression measurements for water and sea water have very good agreement with the Tait and Tait-Gibson equations.
- B and B* values determined by sound velocity at pressure= 1 atm are higher than values of Ekman's by around 20 bars, but they all show the same linearity and slope with respect to salinity.

- Values of B and B* determined by the data of Newton and Kennedy are less than the others values except at temperature= 0ºC.
- By using Ekman and Amagat PVT water data, the Tait equation fits better than the Murnaghan equation.

References

[1] Ahmed, T., 2016. Equations of State and Phase Equilibria, second edition. Gulf Professional Publishing, Elsevier BV, 2016.

[2] Ahmed, T., 2010. Reservoir engineering handbook, fourth edition. Gulf Professional Publishing, Elsevier BV, 2010.

[3] Amagat, E. N., 1893, Elasticite et dilatibilite des fluids: Annales de Chimie et Physique, sere 6, v. 29, p. 68-136; 505-574.

[4] API Research Project 44, 1953. Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, 1953.

[5] Bjerknes, V., and J. W. Sandstrom, 1910. Dynamic meteorology and hydrology, 1, Statics, Carnegie Inst. Washington Publ., 88, 146 pp., 1910.

[6] Crease, J., 1962. The specific volume of sea water under pressure as determined by recent measurements of sound velocity, Deep-Sea Res., 9, 209, 1962.

[7] Del Grosso, V. A., 1952. The velocity of sound in sea water at zero depth, Naval Res. Lab. Rept. 4002, 1952.

[8] DIATI, P., (2020). Reservoir Engineering Lectures, Politecnico di Torino.

[9] Diaz Pena, M., and M. L. McGlashan, 1959. An apparatus for the measurement of the isothermal compressibility of liquid, Trans. Faraday Soc., 55, 2018, 1959.

[10] Dorsey, N. E., 1940. Properties of Ordinary Water Substance, American Chemical Society Monograph Series 81, 673 pp., Reinhold, New York, 1940.

[11] Echeverry, J. & Acherman, S. & Lopez, E., 2017. Peng-Robinson equation of state: 40 years through cubics, Fluid Phase Equilibria, volume 447, 2017.

[12] Ekman, V. W., Die Zusammendrisckbarkeit des Meerwassers, Conseil Perm. Int. l'Explor. de la Mer, Publ. de Circon. 43, Copenhagen, 1908.

[13] Gibson, R. E., and O. H. Loeffier, 1941. Pressure-volume-temperature relations in solutions, 5, The energy-volume coefficients of carbon tetrachloride, water and ethylene glycol, J. Am. Chem. Soc., 63, 898, 1941.

[14] Gibson, R. E., 1935. The influence of the concentration and nature of solution on the compressions of certain aqueous solutions, J. Am. Chem. Soc., 57, 284, 1935.

[15] Harned, H., and B. Owen, 1958. The Physical Chemistry of Electrolytic Solution, 3rd edition, Reinhold, New York, 1958.

[16] Jhaveri, B.S., Youngren, G.K., 1984. Three-parameter modification of the Peng-Robinson equation of sate to improve volumetric predictions. In: Paper SPE 13118, presented at the SPE Annual Technical Conference, Houston, September 16–19, 1984.

[17] Kennedy, G. C., W. L. Knight, and W. T. Holsen,1958. Properties of water, J. Am. Sci., 256, 594, 1958.

[18] Knudsen, 1901. M. H. C., Hydrographische Tabellen, G. E. C. Grad., Copenhagen, 1901.

[19] Murnaghan, F.D., 1944, The Compressibility of Media under Extreme Pressures, Proceedings of the National Academy of Sciences of the United States of America, 30 (9): 244–247, 1944.

[20] Newton, M. S., and G. C. Kennedy, 1965. P-V-V-S relations of sea water, J. Marine Res., 23, 88, 1965.

[21] Peneloux, A., Rauzy, E., Freze, R., 1982. A consistent correlation for Redlich-Kwong-Soave volumes. Fluid Phase Equilib. 8, 7–23, 1982.

[22] Peng, D., Robinson, D., 1976. A NewTwo-Constant Equation of State, Industrial &Engineering Chemistry Fundamentals, 1976.

[23] Redlich, O., Kwong, J., 1949. On the thermodynamics of solutions. An equation of state. Fugacities of gaseous solutions. Chem. Rev. 44, 233–247, 1949.

[24] Sage and Lacey, 1955. Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide and Carbon Dioxide, 1955.

[25] Sage and Lacey, 1950. Thermodynamic Properties of the Lighter Parafin Hydrocarbons and Nitrogen, 1950.

[26] Soave, G., 1993. 20 years of Redlich-Kwong equation of state, Fluid Phase Equilibria, volume82, elsevier science publishers BV, Amsterdam, 1993.

[27] Soave, G., 1972. Equilibrium constants from a modified Redlich-Kwong equation of state, Chemical Engineering Science, volume 27, issue 6, 1972.

[28] Tait, P. G., 1888. Report on some of the physical properties of fresh water and sea water, Rept. Sci. Results Voy. H.M.S. Challenger, Phys. Chem., 2, 1-76, 1888.

[29] Tamman, G., 1934. (See R. E. Gibson, J. Am. Chem. Soc. 56, 4, 1934), or H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, Third Edition, p. 381, Reinhold Publishing Corporation, New York, 1958.

[30] Van der waals, J.D., 1910. The equation of state for gases and liquids, Nobel Lecture, December 12, 1910.

[31] Van der Waals, J.D., 1873. On the Continuity of the Liquid and Gaseous State. Sijthoff, Leiden, The Netherlands (Ph.D. dissertation).

[32] Wilson, W., 1960. Speed of sound in sea water as a function of T, P, and salinity, J. Acoustical Soc. Am., 38, 641, 1960.

[33] Yuan-Hui Li, 1967. Equation of State of Water and Sea Water, Journal of Geophysical Research, volume72, issue10, 1967.

[34] Zudkevitch D., Joffe J., 1970. Correlation and prediction of vapor-liquid equilibria with the Redlich-Kwong equation of state. AIChE J.,16:112-I19, 1970.

[35] Zumdahl, S. S., & Zumdahl, S. A. (2007). Chemistry/Steven Zumdahl, Susan Zumdahl, 2007.

Appendix A: Conversion tables

Pressure

	pa	**bar**	**mm Hg**	**atm**	**psi**	**Ibf/ft^2**	**Kg/cm^2**
pa	1	$1x10^{-5}$	0.007501	$9.8692x10^{-6}$	$1.4504x10^{-4}$	0.020885	$1.0197x10^{-5}$
bar	$1x10^{5}$	1	750.06168	0.986923	14.5038	2088.54	1.0197162
mm Hg	133.3224	$1.3332x10^{-3}$	1	$1.3158x10^{-3}$	0.019337	2.784496	$1.3595x10^{-3}$
atm	101325	1.01325	760	1	14.6959	1.058108	1.0332275
psi	6894.76	0.068948	51.7149	0.068046	1	144	$7.0307x10^{-2}$
Ibf/ft^2	47.8803	$4.788x10^{-4}$	0.035913	$4.7254x10^{-4}$	0.006944	1	$4.8824x10^{-4}$
Kg/cm^2	$9.806x10^{4}$	0.980665	735.559	0.967841	14.2233	2048.16	1

Temperature

	Kelven	**Celsius**	**Fehrenhiet**	**Rankine**
Kelven (K)	1	°C = K-273.15	°F = $\frac{9}{5}$ K-459.67	°R = $\frac{9}{5}$ K
Celsius (°C)	K = °C+273.15	1	°F = $\frac{9}{5}$ °C+32	°R = (°C+273.15) x$\frac{9}{5}$
Fehrenhiet (°F)	K = (°F+459.67) x $\frac{5}{9}$	°C = (°F-32) x $\frac{5}{9}$	1	°R = 459.67+ °F
Rankine (°R)	K = $\frac{5}{9}$ °R	°C= (°R-491.67) x $\frac{5}{9}$	°F = °R-459.67	1

Length

	cm	**m**	**Inch**	**Foot**
cm	1	0.01	0.3937	0.0328
m	100	1	39.37	3.28
Inch (in)	2.54	0.0254	1	0.0833
Foot (ft)	30.48	0.3048	12	1

Mass

	Kg	**Ib**
Kg	1	2.20462
Pound (Ib)	0.45359	1