

# Critical State Behavior of Van der Waal gases & Conformation to Nelson-Obert Characteristics

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**Abstract**— Ideal gas law although widely used has restricted validity as it does not apply to gases which deviate from ideal conditions. Gases in a compressed state can no longer be described by ideal gas law. In this paper we discuss Van der Waal Equation of State which was proposed to account for the shortcomings of ideal gas law. We primarily discuss systems in which real gases are under equilibrium conditions. Compressibility factors for various substances are tabulated and the calculations are validated by accentuating conformance with Nelson-Obert standard compressibility chart. We also present the nature of pressure fluctuation curve with inversion temperatures which can facilitate designing of units meant for systems under phase equilibria.

**Index Terms**— Compressibility Factor, Critical Temperature, Equilibria, Inversion Temperature, Nelson-Obert chart, Real gases, Van der Waal Equation of State.

## 1 INTRODUCTION

IDEAL gas law is amongst the most commonly used laws when dealing with gases. It has widespread applications. It is frequently used to calculate values of molar mass, density, unknown parameters, and also study the effect of change in one parameter on others by use of proportionality. Ideal gases yield commendable results for systems under atmospheric conditions. However, as gases are compressed system behavior deviates from that suggested by the ideal gas law.

This deviation occurs because ideal gas law was formulated after making some assumptions which hold true only under ideal conditions. The ideal gas law makes an assumption that gas particles have no volume of their own. This implies that gas can be compressed to zero or negligible volume which is not true. Not only is it difficult to compress gases beyond a certain stage it also requires huge amounts of energy to do so. Another assumption is that gas particles do not interact with each other. Kinetic energy of gas molecules decreases on cooling; the molecules then interact with each other and this eventually leads to condensation. Condensation can also be achieved by compression for the same reason as molecular interaction increases when they are brought closer. These observations are sufficient to negate the validity of ideal gas law.

In this paper we discuss Van der Waals equation of state describing real gases. We will focus more on the behavior of real gases under equilibrium conditions. We will evaluate compressibility factors and verify their conformation with Nelson-Obert standard compressibility chart. We will also briefly study and calculate inversion temperatures.

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## 2 VAN DER WAAL EQUATION OF STATE (EOS)

Dutch physicist Johannes van der Waals put forth the Van der Waal equation of state (EOS) [1] to account for the molecular interaction and molecular volume. Since, molecules of a gas have their own volume the actual volume of compressed gas is more than the volume estimated by ideal gas law. Van der Waal used the constant  $b$  to indicate the volume occupied by 1 mole of gas and multiplied that with  $n$ , the total number of moles, to account for the volume occupied by all the molecules of the gas. This needs to be subtracted from the actual volume to obtain the ideal volume.

$$\therefore V = V' - nb$$

At higher pressures due to molecular forces of attraction the real gas pressure is lower than ideal gas pressure. Van der Waal fixed this by adding a term to the actual pressure.

$$P = P' + \frac{a n^2}{V^2}$$

*$V, P$  are ideal gas values and  $V', P'$  are real gas values for volume and pressure.*

Ideal gas law is expressed as:

$$PV = nRT$$

The Van der Waal EOS describing ideal gases is as follows:

$$\left( P' + \frac{a n^2}{V^2} \right) (V' - nb) = nRT$$

Where, 
$$a = \frac{27 (RT_c)^2}{64 P_c} \text{ and } b = \frac{RT_c}{8 P_c}$$

### 3 COMPRESSIBILITY FACTOR

#### 3.1 Equilibrium

Although a majority of systems dealt under chemical engineering are not under equilibrium, however, phase equilibria has some important applications including composite synthesis and gas chromatographic analysis [2] among others. Here we calculate compressibility factor, which is a measure of deviation of properties of a gas from ideal behavior for gases, at equilibrium conditions. We also highlight the deviation in compressibility factor between real and ideal gases.

#### 3.2 Real Gases

The compressibility factor for real gases is different from that of ideal gases and it is no longer 1. Values of compressibility factor are calculated in Table 1 and are calculated by:

$$Z = \frac{P'V'}{RT}$$

#### 3.3 Ideal Gases

Van der Waal made adjustments to pressure and volume terms to obtain the equation of state which makes real gases behave similar to ideal gases. The compressibility factor calculated using Van der Waal's EOS will hence be ~1. Values of compressibility factor are calculated in Table 1 and can be calculated by:

$$Z = \frac{PV}{RT} = \frac{\left(P' + \frac{a n^2}{V^2}\right)(V' - nb)}{RT}$$

### 4 CONFORMATION OF Z VALUES WITH NELSON-OBERT STANDARD COMPRESSIBILITY CHART

Nelson-Obert standard compressibility factor chart expresses compressibility factor [3] as a function of reduced pressure for different values of reduced temperature. The reduced pressure and reduced temperature are calculated as given below:

$$P_r = \frac{P}{P_c} \text{ and } T_r = \frac{T}{T_c}$$

Since our study deals with real gases at critical state, the pressure and temperature are  $P_c$  and  $T_c$ , respectively. The reduced parameters hence reduce to unity:

$$P_r = \frac{P_c}{P_c} = 1 \text{ and } T_r = \frac{T_c}{T_c} = 1$$

Nelson-Obert chart presents different values of reduced pressure and reduced temperature but since we are dealing with critical state conditions we will only focus at the curve of  $T_r=1$  vertically above  $P_r=1$ .

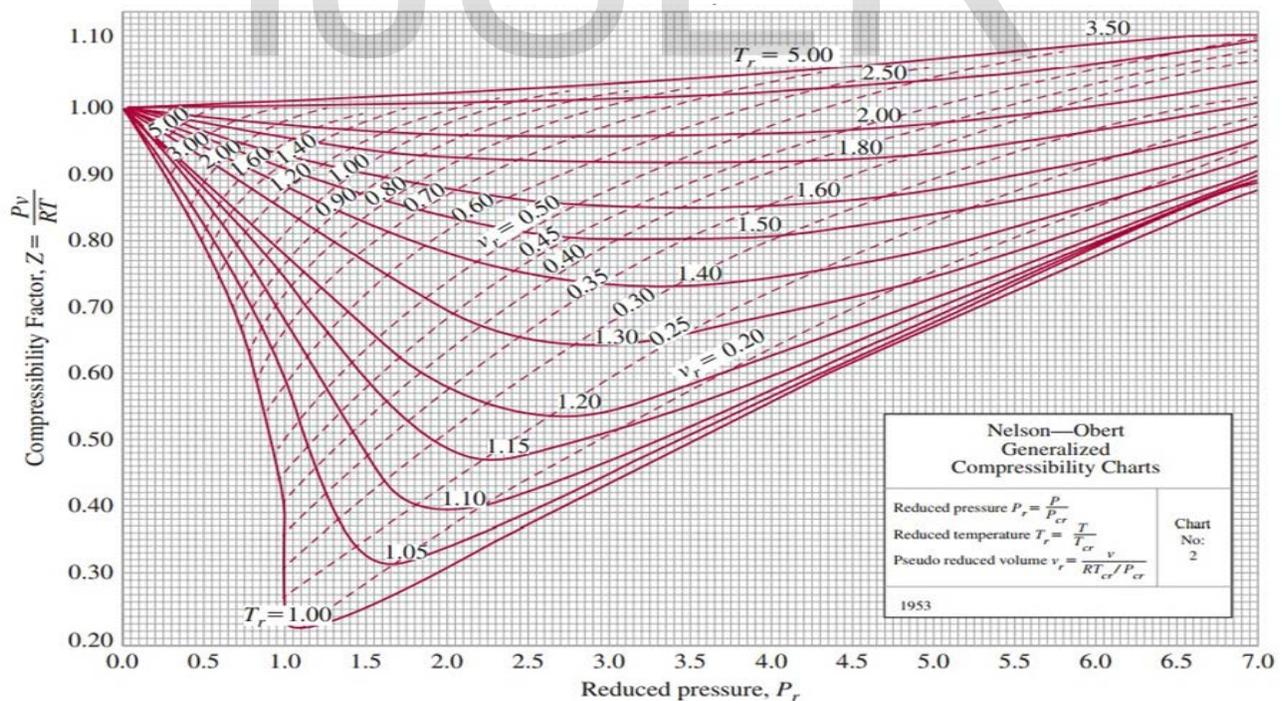


Fig. 1. Nelson-Obert standard compressibility chart

Table 1. Critical state parameters [4] of various substances and calculated Compressibility factor ( $Z_c$ ) values

Substance	Critical Temperature (K)	Critical Pressure (MPa)	Critical Volume ( $m^3/kmol$ )	$Z_c$
Helium	5.3	0.23	0.0578	0.301679
Hydrogen (normal)	33.3	1.3	0.0649	0.304726
Neon	44.5	2.73	0.0417	0.307683
n-Hexane	507.9	3.03	0.3677	0.26383
Nitrogen	126.2	3.39	0.0899	0.290446
Carbon monoxide	133	3.5	0.093	0.294351
Air	132.5	3.77	0.0883	0.30217
n-Butane	425.2	3.8	0.2547	0.273769
Dichlorodifluoromethane (R-12)	384.7	4.01	0.2179	0.273177
Tetrafluoroethane (R-134a)	374.2	4.059	0.1993	0.260009
Propane	370	4.26	0.1998	0.276674
Trichlorofluoromethane (R-11)	471.2	4.38	0.2478	0.277036
Ethane	305.5	4.48	0.148	0.261032
Carbon tetrachloride	556.4	4.56	0.2759	0.271954
Propylene	365	4.62	0.181	0.275545
Methane	191.1	4.64	0.0993	0.289983
Argon	151	4.86	0.0749	0.289939
Benzene	562	4.92	0.2603	0.274074
Oxygen	154.8	5.08	0.078	0.30786
Ethylene	282.4	5.12	0.1242	0.270827
Dichlorofluoromethane (R-21)	451.7	5.17	0.1973	0.271602
Chloroform	536.6	5.47	0.2403	0.294616
Krypton	209.4	5.5	0.0924	0.291893
Xenon	289.8	5.88	0.1186	0.28942
Ethyl alcohol	516	6.38	0.1673	0.24879
Methyl chloride	416.3	6.68	0.143	0.275976
Nitrous oxide	309.7	7.27	0.0961	0.27132
Carbon dioxide	304.2	7.39	0.0943	0.275526
Chlorine	417	7.71	0.1242	0.276188
Sulfur dioxide	430.7	7.88	0.1217	0.267798
Methyl alcohol	513.2	7.95	0.118	0.219851
Bromine	584	10.34	0.1355	0.288544
Ammonia	405.5	11.28	0.0724	0.242227
Water	647.1	22.06	0.056	0.229608

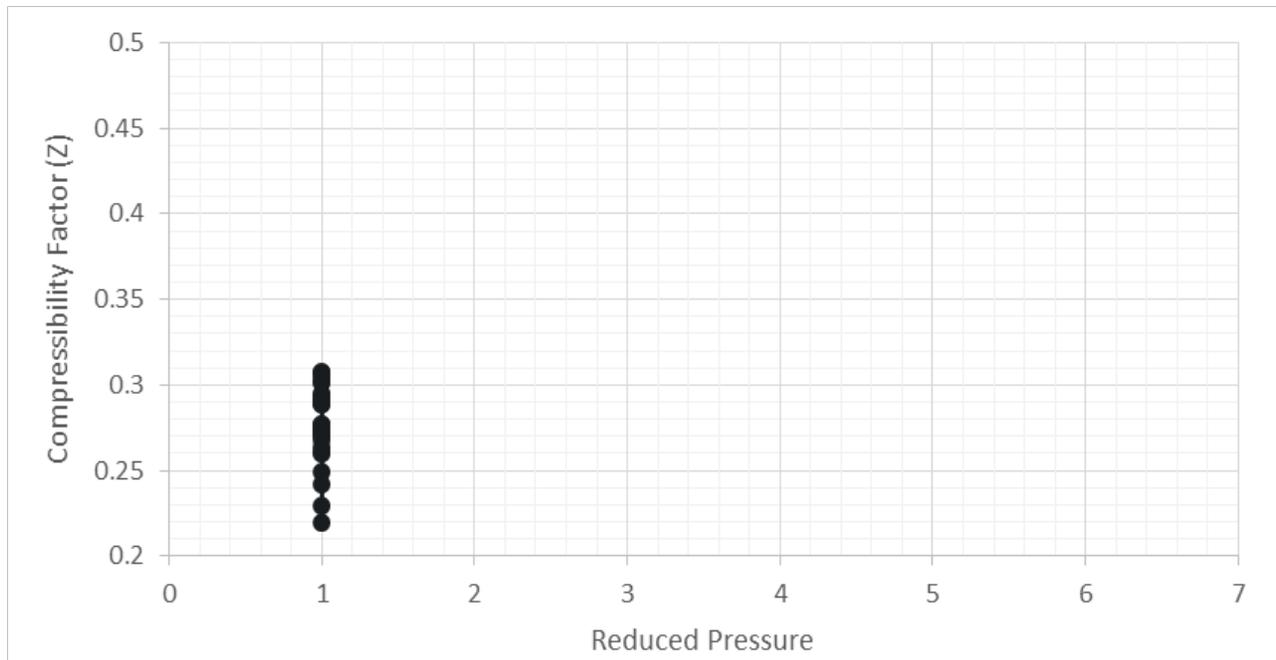


Fig. 2. Compressibility factor vs reduced pressure at critical state showing Nelson-Oberth characteristics

It can be seen from Fig. 2. that compressibility factor can be calculated for fluids at the critical state. It is observed that the calculated compressibility factors are in the range of ~0.22–~0.32. This observation proves that the calculated values for compressibility factors are correct as they conform to the ones provided in the Nelson-Oberth standard compressibility chart. The range of values for compressibility factor is helpful for us as it helps us to predict Z values even when we don't know the exact values of critical state parameters

### 5 INVERSION TEMPERATURE

Inversion temperature is the temperature at which isenthalpic expansion takes place without any change in temperature. On one side of the inversion temperature curve, temperature increases and on the other side temperature decreases. The inversion temperature has its application in heating, cooling and liquefaction of gases. For Van der Waal's gases the inversion temperature ( $T_i$ ) is calculated by:

$$T_i = \frac{27 T_c}{4}$$

Table 2. Inversion Temperatures

Substance	Temperature (K)	Pressure (KPa)	Inversion temperature (K)	ln(Tc)	ln(Ti)	ln(P)
Helium	5.3	230	35.775	1.667707	3.5772	5.43808
Hydrogen (normal)	33.3	1300	224.775	3.505557	5.4151	7.17012
Neon	44.5	2730	300.375	3.795489	5.705	7.91206
n-Hexane	507.9	3030	3428.325	6.230285	8.1398	8.01632
Nitrogen	126.2	3390	851.85	4.837868	6.7474	8.12859
Carbon monoxide	133	3500	897.75	4.890349	6.7999	8.16052
Air	132.5	3770	894.375	4.886583	6.7961	8.23483
n-Butane	425.2	3800	2870.1	6.05256	7.9621	8.24276
Dichlorodifluoromethane (R-12)	384.7	4010	2596.725	5.952464	7.862	8.29655
Tetrafluoroethane (R-134a)	374.2	4059	2525.85	5.92479	7.8343	8.30869
Propane	370	4260	2497.5	5.913503	7.823	8.35702
Trichlorofluoromethane (R-11)	471.2	4380	3180.6	6.155283	8.0648	8.3848
Ethane	305.5	4480	2062.125	5.72195	7.6315	8.40738
Carbon tetrachloride	556.4	4560	3755.7	6.321487	8.231	8.42508
Propylene	365	4620	2463.75	5.899897	7.8094	8.43815
Methane	191.1	4640	1289.925	5.252797	7.1623	8.44247
Argon	151	4860	1019.25	5.01728	6.9268	8.48879
Benzene	562	4920	3793.5	6.331502	8.241	8.50106
Oxygen	154.8	5080	1044.9	5.042134	6.9517	8.53307
Ethylene	282.4	5120	1906.2	5.643325	7.5529	8.54091
Dichlorofluoromethane (R-21)	451.7	5170	3048.975	6.113018	8.0226	8.55063
Chloroform	536.6	5470	3622.05	6.285253	8.1948	8.60703
Krypton	209.4	5500	1413.45	5.344246	7.2538	8.6125
Xenon	289.8	5880	1956.15	5.669191	7.5787	8.67931
Ethyl alcohol	516	6380	3483	6.246107	8.1556	8.76092
Methyl chloride	416.3	6680	2810.025	6.031406	7.9409	8.80687
Nitrous oxide	309.7	7270	2090.475	5.735604	7.6451	8.89151
Carbon dioxide	304.2	7390	2053.35	5.717685	7.6272	8.90788
Chlorine	417	7710	2814.75	6.033086	7.9426	8.95027
Sulfur dioxide	430.7	7880	2907.225	6.065412	7.975	8.97208
Methyl alcohol	513.2	7950	3464.1	6.240666	8.1502	8.98093
Bromine	584	10340	3942	6.369901	8.2794	9.24378
Ammonia	405.5	11280	2737.125	6.005121	7.9147	9.33079
Water	647.1	22060	4367.925	6.472501	8.382	10.0015

The graph shows the nature of inversion temperature, critical temperature, and pressure for various substances. As expected, inversion temperature fluctuates proportional to critical temperature. An interesting observation is nature of pressure variation. Pressure values do not fluctuate rapidly with  $T_c$  and  $T_i$  values. It is seen that the pressure curve doesn't show sharp changes the way  $T_i$  and  $T_c$  curves do. However, this doesn't mean that pressure is independent of these parameters. Peak values of temperatures coincide with that of pressures. When the temperatures experience a sharp fall (in case of hydrogen, helium, and neon) the pressure curve also drops. Similar behavior is observed at the other end of the graph where pressure curve rises along with rise in temperatures.

This observation is significant as it suggests that systems which have multiple gases under equilibrium (multicomponent systems) will exhibit greater fluctuations in temperature as compared to pressure. This helps us in designing better storage tanks or reactors for multicomponent systems under equilibrium.

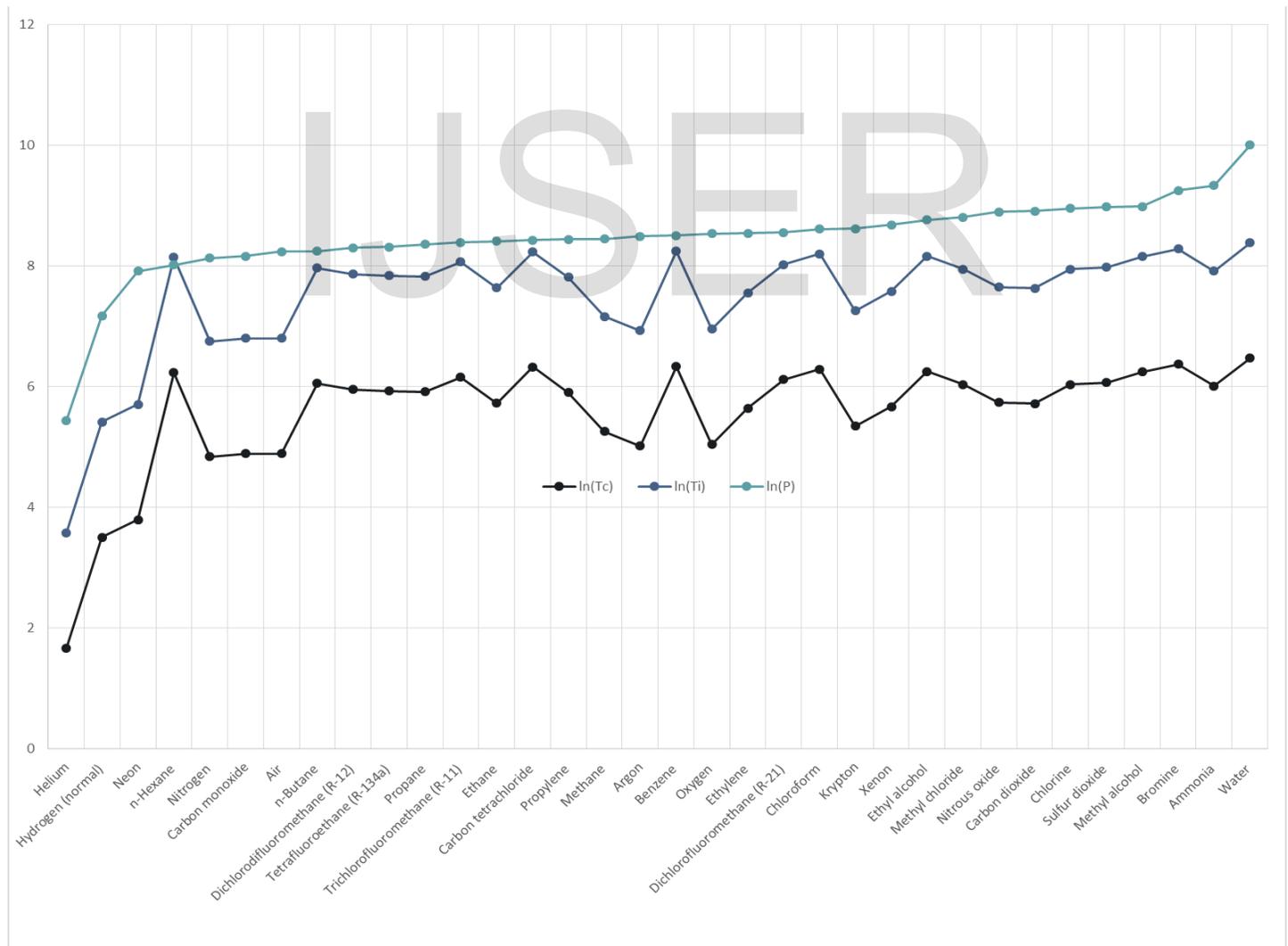


Fig. 3. Correlation between nature of inversion temperature, critical temperature and pressure curves

#### 4 CONCLUSION

It is important to understand the behavior of real gases as ideal gas law doesn't accurately represent a system under non-ideal conditions such as a compressed state. Critical state and equilibrium conditions have received much interest as these have some important applications like gas chromatographic analysis, composite synthesis, mass diffusion [5] among others. This paper was written with the intention of shedding some light on critical state properties and behavior of Van der Waal (real) gases to aid those applications.

#### ACKNOWLEDGMENT

The authors would like to thank their families for being a pillar of support for them, thereby enabling them to put forth this paper.

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