

Two Simple yet Accurate Equations for Calculating the Fugacity Coefficient Phi and the Gas Compressibility Factor Z.

by A.E. for mychemengmusings.wordpress.com

In this post two new powerful equations are presented one for the Gas Compressibility Factor 'Z' and one for the Gas Fugacity Coefficient 'phi'. Both give excellent prediction results for the sub-critical reduced pressure region and superheated vapor region. These two equations are surprisingly simple, allow direct calculation without the need for iterations hence easy to implement in spreadsheets or used on handheld devices and calculators! The two form a thermodynamically consistent pair. Three Charts have been prepared mapping out the predictions made with these equations.

Numerical calculation examples are given including for superheated Steam, Ethane, Propane and Propylene.

The basis for each of these equations is presented in Part III of this post giving ample attention to the basis on which these equations rest and their validation against measured data.

The first new equation for the gas fugacity coefficient 'phi' is stated in the form of a corresponding states correlation for the reduced pressures ranging from $0 \leq Pr \leq 2$ and reduced temperatures ranging between $0.9 \leq Tr \leq 2$. The Phi isotherms show a linear dependency on the reduced pressure! Usually the gas fugacity coefficient 'phi' is obtained by laborious (programmed) calculations using equations of state (EOS) like the Soave-Redlich-Kwong (SRK) or the Peng-Robinson (PR) or other elaborate (sets of) equations. This new equation's predictions are within 0.4% of the Hougen - Ragatz Chart.

The second new equation presented in this post is a new and surprisingly simple *formulation* of the Gas Compressibility factor Z and its dependence on reduced temperature Tr and reduced pressure Pr! It is based on- and has been derived from the new equation for 'phi'. Whereas the common route to obtain values for the compressibility factor Z is via equation of state formulations such as the "van der Waals" (vdW) equation or one of its sophisticated derivative formulations such as the SRK and the PR EOS, the new formulation for Z presented uses the thermodynamic 'definition' of phi in reverse.(see part III below). In addition Part III also describes a new conceptual model for the compressibility factor Z of a *real gas* that gives a theoretical, conceptual underpinning of the form of equation for Z as arrived at via the linear equation of 'phi'. This post is divided in three parts:

PART I The Two Equations

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PART III The Basis for the Two Equations

Part III -a the basis for the new fugacity coefficient's correlation.

Part III -b the basis for the new gas compressibility Factor Z equation.

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Appendix -A Table: Comparison of Z-pbe equation with Lydersen data.

Appendix -B The 'marked up' Hougen – Ragatz Chart.

A pdf version of this post is given [here](#)

PART I The Two Equations

Part I -a The Gas Fugacity Coefficient 'Phi' correlation.

Please note the formula's given below are in 'excel' style notation using as multiplication symbol ' * ' and for an exponent (raising to the power) the symbol ' ^ '.

The gas fugacity coefficient 'phi' is equal to 1 for very low pressures. Consequently, for example, in volatility calculations the fugacity, being the product of the fugacity coefficient and the absolute pressure, equals the absolute (partial) pressure of the substance or compound.

For low to moderately high pressures, say for reduced pressure from 0.1 to 1 or 2, the thermodynamically effective pressure, the fugacity 'f', is lower than the measured absolute gas pressure P: $f = \text{phi} * P$ in which $\text{phi} < 1$.

The following equation in *corresponding states* format allows you to directly calculate phi :

$$\text{Phi} = 1 - 0.333 / \text{Tr}^{3.905} * \text{Pr} \dots\dots\dots(\text{Eq. I-1})$$

in which Tr is the reduced temperature equal to T / T_{crit} and Pr the reduced pressure equal to P / P_{crit} . This correlation is based on generalized data with $Z_c = 0.27$; this correlation is valid for $0.9 \leq \text{Tr} \leq 2$ and $0 < \text{Pr} < 1.5 - 2$.

The average percentage error in the calculated results is 0.41 % compared to the Hougen – Ragatz Chart (see Appendix).

For clarity sake I will repeat the above formula in "math type formula format" (in pdf only)

$$\varphi = 1 - \frac{0.333}{T_r^{3.905}} \cdot P_r \dots\dots\dots(\text{Eq. I-1})$$

Part I -b The Gas Compressibility Factor Z new equation "Z-pbe".

The gas compressibility factor Z signifies the degree a 'real' gas deviates from an 'ideal' gas. For a real gas the compressibility factor is in most cases smaller than 1, reflecting the fact that intermolecular attraction forces do reduce the volume the gas exhibits for a given set of pressure and temperature conditions ($Z = V\text{-real} / V\text{-ideal}$).

The following equation was derived from the above fugacity correlation (see Part III -b). It is a surprisingly simple and explicit equation that allows direct calculation of the Z factor without the need for iterative calculations, easy to implement in an excel spread sheet as a 'single cell' formula and no need for the 'solver' tool in excel :

$$Z = 1 - (0.333 * \text{Pr} / \text{Tr}^{3.905}) / (1 - 0.333 * \text{Pr} / \text{Tr}^{3.905}) \dots\dots\dots(\text{Eq. I-2})$$

in which: 'Tr' is the reduced temperature and 'Pr' is the reduced pressure.

This equation is valid for the following conditions: $0 < \text{Pr} \leq 1$ and $0.9 < \text{Tr} < 2$.

It predicts compressibility factor Z values with excellent accuracy of 0.41 % compared to the Lydersen measured data ($Z_c = 0.27$).

For clarity sake I will repeat the above equation in 'math type formula' format (in pdf only)

$$Z = 1 - \frac{0.333 / T_r^{3.905} \cdot P_r}{1 - 0.333 / T_r^{3.905} \cdot P_r} \dots\dots\dots(\text{Eq. I-2})$$

It is interesting to note that Eq. I-2 not only has a semi-empirical basis, but can be developed along theoretical lines with the conceptual model described in Part III –c !

Part I -c Graphical representations of these two equations.

The Gas Fugacity Coefficient Φ Equation (Eq.I-1) calculation results have been plotted on a semi-logarithmic scale versus the reduced pressure 'Pr' in the following Chart (click to enlarge):

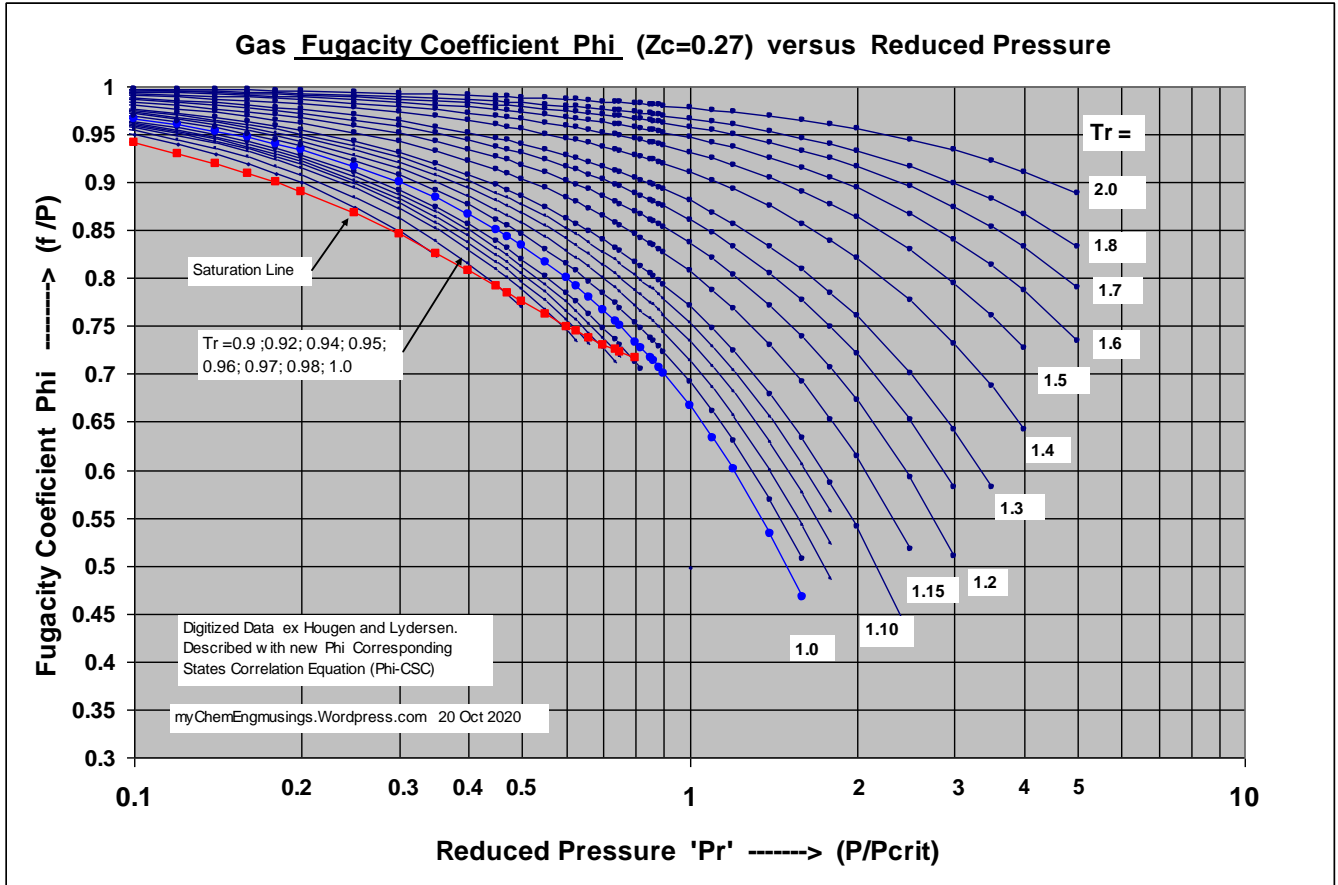


Fig 1. The isotherms of the fugacity coefficient phi versus log Pr from Eq.I-1.

Note how the *isotherms of Φ* , that according to Eq.I-1 are linear in P_r , present themselves as curved lines on the semi-log plot (compare the Hougen – Ragatz Chart in Appendix -B).

The new Compressibility Factor Z -pbe (Eq.I-2) versus the reduced pressure P_r plotted on linear scales for $P_r < =1$.

In the next Chart of Fig. 2 the gas compressibility factor Z calculated with Eq.I-2 (Z -pbe) has been plotted as follows (click on Chart to enlarge):

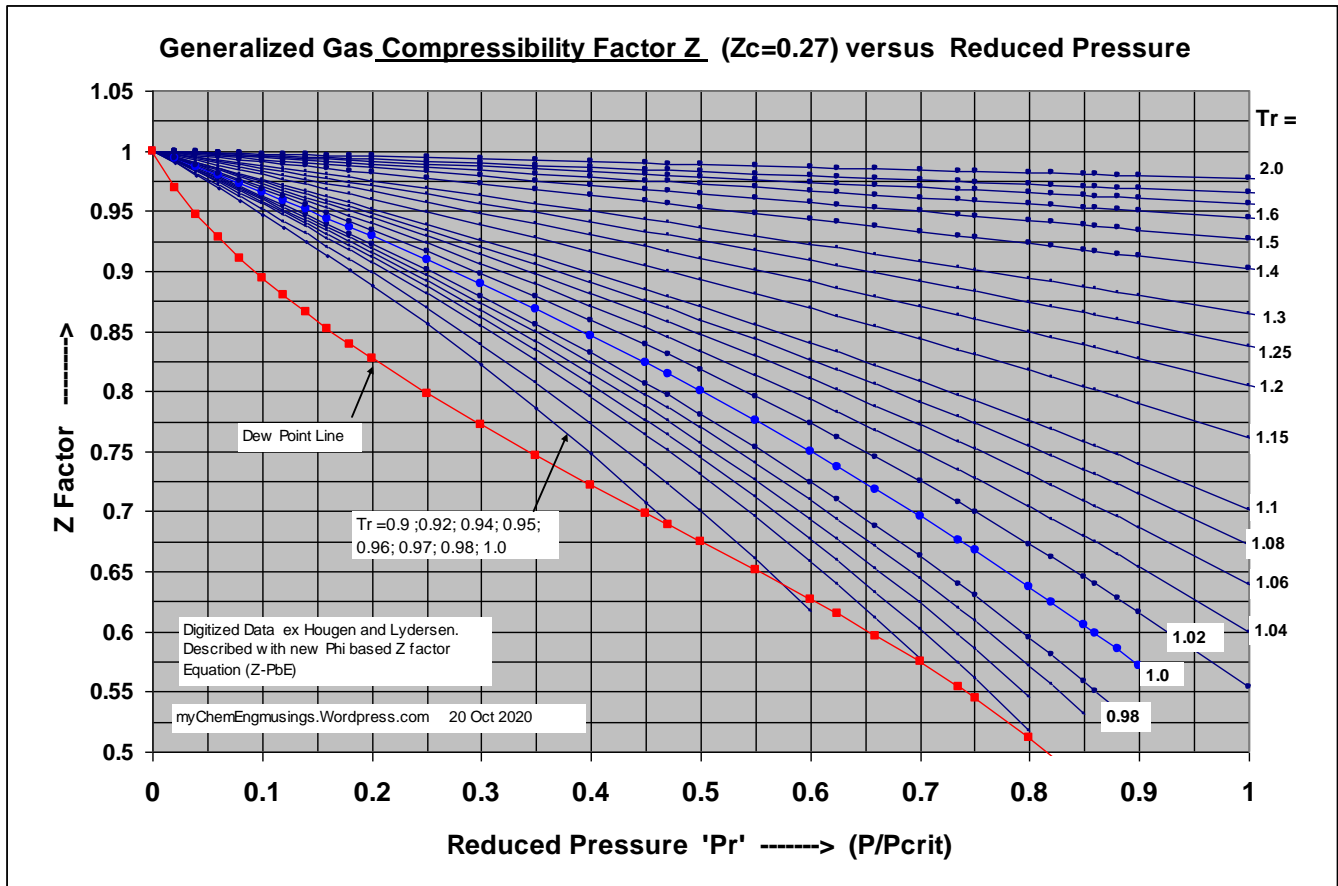


Fig 2. Isotherms of 'Z' by the new compressibility factor Z equation Eq. I-2 (Z-pbe).

Note how the *isotherms of Z* according to Eq. I-2 show themselves on this linear plot as slightly curved with downwards sloping lines.

The predictions with the Z-pbe equation for Z (Eq. I-2) have been compared to the digitized data from the Lydersen Chart that is based on measured data. I found for the reduced pressure range of $0 < Pr <= 1$ that the average percentage error was 0.41 % .

The comparison with Lydersen's data has been further extended to reduced pressures above the critical point to check to what extent the Z-pbe equation's predictions hold up. In addition its predictions were compared to values obtained from the Soave-Redlich-Kwong (SRK) EOS (See Table in Appendix -A for details). These comparisons have shown that its predictions for reduced pressures above ($Pr \geq 1$) still give reasonably accurate results as long as the isotherms for Z are not too closely approaching their inflexion points between the falling and rising of the isotherm. The eventual rising of the Z values at higher reduced pressures ($Pr \gg 1$) can be explained by the repulsive intermolecular forces to become dominating the fluid 's P-V-T behavior.

Therefore it is of interest to also plot the values predicted with the Z-pbe equation (Eq. I-2) on a semi-logarithmic plot with the reduced pressure ranging from 0.1 to 10 and plot them to

the extent of their range that still give reasonable good predictions (see Table in Appendix -A for error%).

The new Compressibility Factor Equation 'Z-pbe' (Eq. I-2) versus the reduced pressure P_r plotted on a semi logarithmic scale .

The calculated Z isotherms from Eq. I-2 are shown in the next Chart up to the pressure level where the approach to the inflexion point starts to diminish the predictions' accuracy.

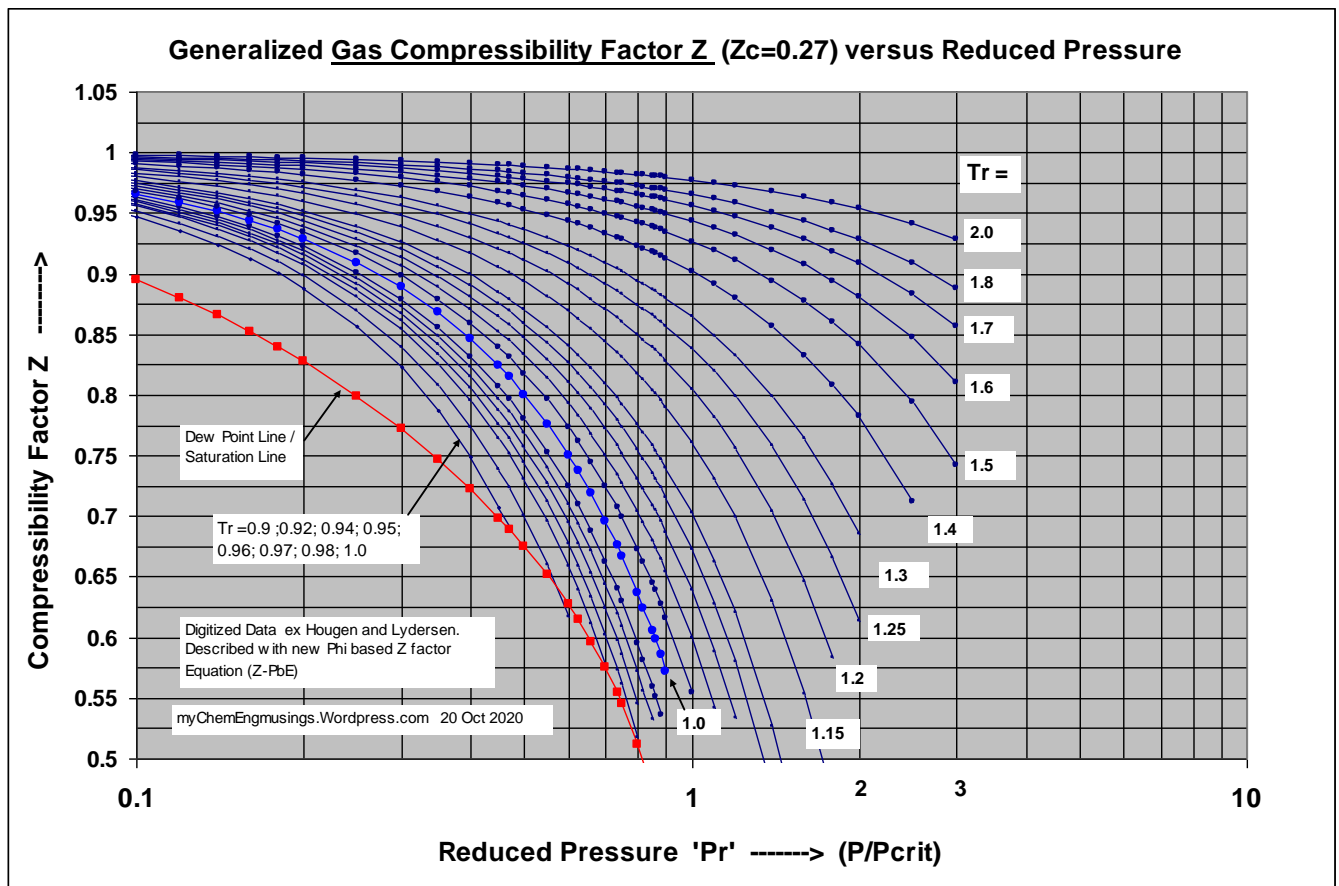


Fig 3. Semi-log plot Isotherms of the new compressibility factor Z equation (Z-pbe).

See Part II -b for numerical examples and comparisons with Lydersen data and predictions from the SRK and PR equations of state ! A more complete comparison table giving percentage of error% determination is shown in the Appendix.

PART II Numerical Calculation Examples

Part II -a Numerical Examples for the Fugacity Coefficient Phi

1. Gas Fugacity Coefficient Phi for pure compounds. Example calculations.
Example 1. For pure STEAM at 300 oC and 70 Bar abs.

> Critical properties of Water: $T_c = 647.1 \text{ oK}$; $P_c = 220.6 \text{ Bar abs}$
 > Reduced Temperature $Tr = (300+273.15)/ 647.1 = 0.8857$
 > Reduced Pressure $Pr = 70 / 220.6 = 0.3173$
 ==> Fugacity Coefficient $\Phi = 1 - 0.333/ 0.8857^{3.905} * 0.3173 = \underline{0.830}$
 Comment : ϕ obtained from PR EOS: $\phi = 0.828$; SRK EOS: $\phi = 0.839$

Example 2. For STEAM at 500 oC and 140 Bar abs.

> $Tr = 1.1948$ and $Pr = 0.6346$
 ==> Fugacity Coefficient $\Phi = 1 - 0.333/ 1.1948^{3.905} * 0.6346 = \underline{0.895}$
 Comment : ϕ obtained from PR EOS: $\phi = 0.877$; SRK EOS: $\phi = 0.894$

Example 3. For ETHANE at 25 oC and 50 Bar abs

> Critical properties of Ethane: $T_c = 305.43 \text{ oK}$; $P_c = 48.8 \text{ Bar abs}$
 > Reduced Temperature $Tr = (25+273.15)/ 305.43 = 0.9762$
 > Reduced Pressure $Pr = 50 / 48.8 = 1.0246$
 ==> Fugacity Coefficient $\Phi = 1 - 0.333/ 0.9762^{3.905} * 1.0246 = \underline{0.625}$
 Comment : ϕ obtained from PR EOS: $\phi = 0.581$; SRK EOS: $\phi = 0.602$

Example 4. For PROPANE at 85 oC and 30 Bar abs

> Critical properties of Propane: $T_c = 369.9 \text{ oK}$; $P_c = 42.57 \text{ Bar abs}$
 > Reduced Temperature $Tr = (85+273.15)/ 369.9 = 0.9862$
 > Reduced Pressure $Pr = 30 / 42.57 = 0.7047$
 ==> Fugacity Coefficient $\Phi = 1 - 0.333/ 0.9862^{3.905} * 0.7047 = \underline{0.734}$
 Comment : ϕ obtained from PR EOS: $\phi = 0.721$; SRK EOS: $\phi = 0.740$

Example 5. For PROPYLENE at 85 oC and 30 Bar abs

> Critical properties of Propylene: $T_c = 365 \text{ oK}$; $P_c = 46.2 \text{ Bar abs}$
 > Reduced Temperature $Tr = (85+273.15)/ 365 = 0.9812$
 > Reduced Pressure $Pr = 30 / 46.2 = 0.6494$
 ==> Fugacity Coefficient $\Phi = 1 - 0.333/ 0.9812^{3.905} * 0.6494 = \underline{0.767}$
 Comment : ϕ obtained from PR EOS: $\phi = 0.753$; SRK EOS: $\phi = 0.771$

Part II -b Numerical Examples for the Compressibility Factor Z (Eq. I-2)

Equation I-2 is derived from the correlation found for the fugacity coefficient (Eq. I-1) that is based on the generalized Hougen - Ragatz Chart valid for compounds with $Z_c = 0.27$. (see derivation in PART III -b). In the numerical calculation examples given here I will in addition verify the results for the Z values obtained against the measured data of Lydersen *et al*. In addition also a comparison is done with the results generated by the SRK EOS taking n-Pentane as "model" compound as its critical Z factor is very close to 0.27 and to be precise: 0.269.

Example 1. Calculations & comparison with Lydersen 's measured data
Given the following reduced Temperature T_r and reduced Pressures P_r :

T_r	P_r	Z-phi based equation (Eq.I-2)	Lydersen	Error%
0.94	0.3	$Z\text{-pbe} = 1 - \frac{(0.333/0.94^{3.905} * 0.3)}{(1 - 0.333/0.94^{3.905} * 0.3)} = 0.8543$	0.855	0.1%
0.98	0.7	$Z\text{-pbe} = 0.6627$	0.6685	0.9%
1.10	1.0	$Z\text{-pbe} = 0.7021$	0.701	0.2%
1.30	0.8	$Z\text{-pbe} = 0.8943$	0.8893	0.6%

Example 2 n-Pentane ($Z_c = 0.269$; $T_c = 469.6$ oK ; $P_c = 33.74$ Bar abs)

For temperature & Pressure conditions of

Pressure	Temperature	P_r	T_r	$Z\text{-pbe}$	$Z\text{-Lydersen}$	$Z\text{-SRK}$
13.50 Bara	187.1 oC	=0.40	=0.98	= 0.8316	= 0.8325	= 0.8363
26.99 Bara	196.5 oC	=0.80	=1.0	= 0.6369	= 0.6370	= 0.6388
26.99 Bara	337.3 oC	=0.80	=1.3	= 0.8943	= 0.8893	= 0.8989

Example 3 Superheated Steam ($Z_c = 0.2294$; $T_c = 647.1$ oK ; $P_c = 220.6$ Bar abs)

Pressure	Temperature	Deg.Super	P_r	T_r	$Z\text{-pbe}$	$Z\text{-steamTable}$
140 Bara	550 oC	213 oC	= 0.6345	= 1.272	= 0.910	= 0.912
140 Bara	375 oC	37.5 oC	= 0.6345	= 1.002	= 0.734	= 0.724
60 Bara	400 oC	125 oC	= 0.2719	=1.040	=0.9158	=0.915

It is worth noting for the example of Superheated Steam that notwithstanding the fact that the Z_c value for Water (0.229) is significantly smaller than $Z_c = 0.27$ on which the fugacity and the $Z\text{-pbe}$ equation are based, nevertheless we find that good results are obtained in practice. Why ? Because the greater the degree of superheat of the vapor the farther away removed from the critical conditions the less influence " Z_c " has on the increasing degree of ideality of the vapor!

PART III Basis for the two equations.

Part III –a The equation for The Gas Fugacity Coefficient 'Phi '.

You perhaps may have wondered why I started this post with the Gas Fugacity Coefficient first and not with the Gas Compressibility Factor Z ? In thermodynamical treatises or lectures the Equations of State expressed in the form of an equation in " Z " are usually dealt with first followed later by the subject of Fugacity (thermodynamically active pressure) and the Gas Fugacity Coefficient 'phi '.

The connecting and defining equation between the two reads as :

$$\ln(\phi) = \int_0^P \frac{(Z-1)}{P} \cdot d(P) \quad \text{for Constant } T$$

$\ln(\phi) = \text{def. Integral } 0 \text{ to } P \text{ of } [(Z-1) / P] dP \quad \text{for constant } T$

from this integration result the fugacity coefficient “phi “is obtained, allowing the Fugacity “ f “ to be calculated as $f = \phi * P$.

In general ‘phi ‘ can be obtained in one of two ways. If you have an analytical expression for Z , for example from an EOS, then via the above defining integral expression ‘phi’ maybe obtained. However depending on the complexity of the equation or correlation for ‘Z’ as function of temperature and pressure, performing this integration to obtain an analytical expression for the integral may be difficult or prove impossible. Alternately, if you have measured data for ‘Z’ as function of P and T you can do a graphical integration by determining the area under the plot of Z-1 values along an isotherm versus pressure.

The Zv correlation

Having developed the Zv correlation as function of reduced temperature and reduced pressure (see earlier post). I was attempting to find an expression for the corresponding ‘phi’ based on that correlation. However as you can see for yourself integration of this equation is not straight forward to say the least. Next I checked out what form of equation ‘phi’ takes when based on the different equations of state (vdW, SRK, PR) as you can observe yourself these integrations have been performed but are rather elaborate and complex.

The Hougen – Ragatz Chart for Phi versus Pr

Following this, I turned to the Hougen -Ragatz Chart with plots of ‘phi’ versus reduced pressure Pr for various isotherms of Tr (see Appended Chart). When digitizing data points along a series of isotherms (for Tr of 0.90 to 2) and simply plotting the data against a linear Pr scale, I was in for a surprise: all the way up to fairly high reduced pressures Pr , even beyond Pr =1, the ‘phi’ values showed as a precise *straight* line versus Pr! Not something to be surmised when looking at the Hougen – Ragatz Chart that uses a semi-logarithmic plot of phi versus Pr ranging over three decades from 0.1 to 100 !

In the Table below the linear regression results for equation ‘ $\Phi = A - B * Pr$ ‘ I obtained are given for the isotherms listed:

Table Regression Results

<u>Tr =</u>	<u>A =</u>	<u>B=</u>	<u>Pr from</u>	<u>r^2</u>
2.0	0.999	0.0232	0.1 - 2	0.9950
1.8	1.001	0.0321	0.1 - 2	0.9955
1.5	0.9993	0.0682	0.1 - 2	0.9988
1.4	0.9991	0.0885	0.1 - 2	0.9996
1.3	1.0025	0.1250	0.1 - 2	0.9987
1.25	1.002	0.1440	0.1 - 2	0.9984
1.20	1.004	0.1650	0.1 - 2	0.9989
1.15	1.0022	0.1956	0.1 - 2	0.9975
1.10	1.0052	0.2292	0.1 - 2	0.9985
1.00	1.0078	0.3293	0.1 - 2	0.9907
1.00	1.0128	0.3337	0.1 -1.0	0.9977

Obviously the constant 'A' equals 1.000 as for Pr = 0 the theoretical expectation is Phi = 1.000. The constant 'B' was correlated with Tr as : $1/B = 3 \cdot Tr^{3.905}$ and hence we obtain for the fugacity coefficient 'phi' the relation:

$$\text{Phi} = 1 - 0.333 / \text{Tr}^{3.905} \cdot \text{Pr} \quad ; \text{ this is the equation reported in Part I as Eq. I-1}$$

This is a remarkable simple equation for the fugacity coefficient. Granted it covers obviously only the left hand side of what appears in the Hougen – Ragt Chart as isotherms shaped in the form of a “bathtub curve“ extending over the three decades of Pr !

This equation for 'phi' is very handy and useful for the low to moderately high reduced pressure range!

Part III –b The equation for The Gas Compressibility Factor Z (Z-pbe) .

This section of Part III describes how a new equation for the compressibility factor Z based on the phi equation was arrived at, which equation I have labeled as the “Z-pbe“ equation. Contemplating this very simple equation for 'phi' then immediately the question rose in my mind what kind of 'Z equation' gives rise to such simple equation for 'phi' ?

Asking myself: can you find an answer by reversing equation III-1 ? Yes , by realizing that:

$$\frac{d\text{Ln}(\phi)}{dP_r} = Z - 1 \quad \text{and substituting} \quad \frac{d\text{Ln}(1 - 0.333 / T_r^{3.905} \cdot P_r)}{dP_r} = Z - 1$$

this gives:

$$Z = 1 - \frac{0.333 / T_r^{3.905} \cdot P_r}{(1 - 0.333 / T_r^{3.905} \cdot P_r)} \quad ; \text{ see equation Eq. I-2}$$

Having never ever seen an expression or equation for the gas compressibility factor Z like this one, then the question became: how good is it in predicting Z values?

And the answer I found was: beyond expectation, very good!

Having available the digitized data for Lydersen, an evaluation of its predictions against the Lydersen data showed that the *average percentage error is 0.41%* for the following conditions $0 = < Pr <= 1$ with $0.90 = < Tr <= 2$.

Interestingly I found furthermore this equation still gives reasonable results for a limited range of super-critical pressures ($Pr > 1$; see validation calculations and checklist in the Appendix -A).

Having said that the equation for 'phi' is remarkable and simple, I would certainly say the very same for this new compressibility factor equation. I will refer to this equation and its predictions as the *phi based equation* "Z-pbe". Note that these two equations together form a (thermodynamically) consistent pair.

But wait there is something more to notice about equation (Eq. 1-2). The fraction part of this equation reminds me of a formula in physics that looks very similar in form and shape! Which one? Answer: the 'Langmuir equation' that describes the process of adsorption of a compound (the adsorbate) on a solid substrate (the adsorbent). If we "see" the factor "0.333/Tr^{3.905}" as a temperature dependent equilibrium constant 'Keq' then, as you can see for your self, this fraction looks very much similar as:

$$\frac{K_{eq} \cdot P_r}{(1 - K_{eq} \cdot P_r)}$$

How was the theoretical 'Langmuir' equation arrived at? Can I try to develop a model for the compressibility factor Z as well? The answer is yes (!) as explained in the following section.

Part III –c The Conceptual Model for the Real Gas Compressibility Factor Z.

The state of an ideal gas can be described by a combination of two *intensive* variables ("P" and "T") plus two *extensive* variables (the number of kmoles "N" and the volume "V").

$$P \cdot V = N \cdot R \cdot T$$

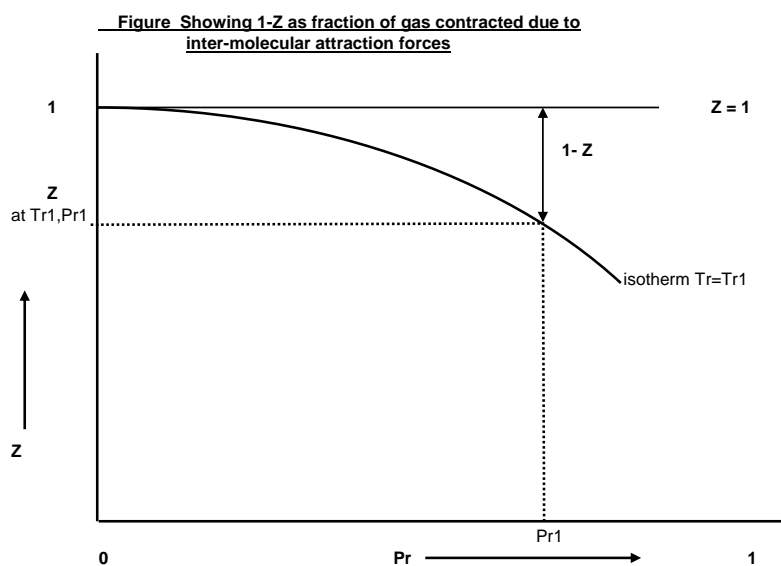
The state of any gas, real or ideal, can be described by a combination of two intensive variables (P and T) plus two extensive variables *plus the compressibility factor "Z"*.

$$P \cdot V = N \cdot Z \cdot R \cdot T$$

in which 'Z' is a dimensionless factor that accounts for the *degree of non-ideality* of the gas. With Z=1 it reflects that the real gas behaves *as if it is an ideal gas* in which only kinetic energy of the gas particles is dominant and necessary to be taking into account to describe its behavior and any attraction forces between particles can be and are ignored! Hence we can see the Z factor as reflective of the interplay, the balance between the kinetic energy and the potential energy (the attraction forces) in the accounting for its behavior. In analogy with the Langmuir approach let us conceive of the state of a real gas at a given reduced pressure Pr and temperature Tr not as a static "(macro-) state" but as a *dynamic (micro-) equilibrium* state. Just as Langmuir considers two 'species' interacting with each other and establishing an equilibrium, that is between the adsorbate molecules and the 'sites' on the solid that are capable of attracting these molecules.

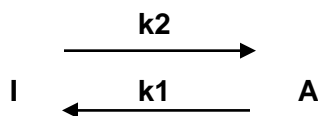
In an analogous fashion we can conceive of a real gas as of consisting of two types of gas particles (atoms, molecules) present in the gas (mixture) : on the one hand there are particles behaving as ideal gas i.e. unaffected by inter-particle attractive forces and on the other hand there are the ones that are affected, that are “under the influence” of the mutually attracting inter-molecular forces. If we remember the ‘kinetic gas theory’ saying that the velocity of gas particles is not uniform but there exists even in the ideal gas state a whole distribution of velocities (Maxwell). Some have high velocity some low. The gas temperature, as macro- property, is a measure for the average kinetic energy of the gas. Refreshing our memory thus, it helps us to conceive of the simultaneous presence of ideal gas like behaving, high velocity particles and gas particles at the low end of the distribution that are or potentially can be under the influence of the mutual attraction force (field).

If we look at the following sketch of Z values along an isotherm plotted against reduced pressure



we can see that the fraction of the total of gas particles that (on average) are undergoing attraction is indicated by the value of ‘1-Z’ at the conditions of $T_r=Tr1$ and $Pr=Pr1$. This fraction thus is a function of Pr and Tr ! The lower the temperature and the higher the pressure the less the number of particles that are able to move like ideal gas particles.

Consider an amount of N kilomol gas at reduced temperature and pressure conditions T_r and Pr . Then at equilibrium a number of particles “ I ” behave as ideal gas while the remainder of particles behave as ‘attracted or associated gas “ A ”:



or this equilibrium described in words a number of “ideal-behaved” gas particles ‘I’ are in dynamic equilibrium with the number of particles that are “attraction-behaved” : ‘A’ thus those that also possess potential energy.

the rate of formation of 'A' is: $dN_a / dt = k_2 \cdot N_i \cdot P_r$

and the reverse rate of forming 'I' is $dN_i / dt = k_1 \cdot N_a$

We can write these also in terms of the fractions of the total number N as: $n_a = N_a / N$ and $n_i = N_i / N$. and thus $n_a + n_i = 1$.

at equilibrium the reverse formation of 'I' equals the forward formation rate of 'A'

$$k_1 \cdot n_a = k_2 \cdot n_i \cdot P_r$$

dividing by k_1 and substituting $(1 - n_a)$ for n_i we get :

$$n_a = k_2 / k_1 \cdot (1 - n_a) \cdot P_r$$

defining k_2/k_1 as the equilibrium constant K_{eq} we find for n_a :

$$n_a = \frac{K_{eq} \cdot P_r}{(1 - K_{eq} \cdot P_r)}$$

With this equation we have found an expression that describes the fraction of gas particles 'na', that are influenced by mutual attraction in a gas at equilibrium at P_r and T_r , in terms of reduced gas pressure and the equilibrium constant K_{eq} .

Having pointed out above that 'na' is equal to '1- Z', thus we find:

$$Z = 1 - \frac{K_{eq} \cdot P_r}{(1 - K_{eq} \cdot P_r)}$$

This equation is identical to the equation that was derived in section Part III –b which was arrived at via an entirely different route, viz. the route starting with measured data for the gas fugacity coefficient 'phi' and so on ! In general the equilibrium constants are a sole function of reduced temperature !

And with this equation we have developed a model for the compressibility factor Z based on the conception of (any) real gas as an aggregate of gas particles some of which behave as if in an ideal gas (only kinetic energy) and some others behave as in a gas where attraction forces (van der Waals' forces) come into play and determine their behavior! These two groups of gas particles are in a dynamic equilibrium for a given (static) pressure and temperature!

I will call this equation the "Zeq" equation because it will allow the equilibrium constant 'Keq' to be explicitly written as a function of P_r and together with a set actual measured Z value data and determine the dependency of this constant as a function of reduced temperature T_r .

$$K_{eq} = \frac{(1 - Z)}{P_r(2 - Z)}$$

to determine how the temperature function can be improved and extended to cover the low temperature region below $T_r = 0.9$! (t.b.d.)

====Appendices begin on the next page ===

APPENDIX -A

COMPARISON AND VALIDATING THE " Z-pbe" EQUATION

COMPARISON OF THE ' Z-pbe ' EQUATION PREDICTIONS

With the measured data (digitized) of LYDERSEN
(generalized for $Z_c = 0.27$)

FOR REFERENCE Z-pbe values compared with Z-SRK values n-Pentane as model compound

Model Component: n-Pentane $Z_c = 0.269$

n-Pentane Critical Data (APIDATABASE)

Tc (oK) = 469.6 Pc (Bara) = 33.74

===== N-Pentane =====

<u>Tr</u>	<u>Pr</u>	<u>Z-phibased</u> <u>Z-pbe</u> <u>calc Eq. 2</u>	<u>Lydersen</u> <u>Chart</u> <u>measured</u> <u>digitiz. Data</u>	<u>Error%</u>	<u>T oK</u>	<u>P bara</u>	<u>Z -SRK EOS</u>	<u>Z-pbe diff.%</u>	
0.9	0.1	0.9471	0.9455	0.2	422.64	3.37			
0.9	0.2	0.8883	0.890	0.2	422.64	6.75	0.8879	0.0	
0.9	0.3	0.8225	0.828	0.7	422.64	10.12	0.8239	0.2	
0.9	0.4	0.7484	0.763	1.9	422.64	13.50	0.7509	0.3	
0.94	0.2	0.9073	0.907	0.0	441.42	6.75	0.9030	0.5	
0.94	0.3	0.8543	0.855	0.1	441.42	10.12	0.8494	0.6	
0.94	0.4	0.7958	0.800	0.5	441.42	13.50	0.7906	0.7	
0.94	0.5	0.7310	0.734	0.4	441.42	16.87	0.7243	0.9	
0.94	0.6	0.6588	0.6566	0.3	441.42	20.24	0.6448	2.2	
0.96	0.2	0.9153	0.9156	0.0	450.82	6.75	0.9174	0.2	
0.96	0.3	0.8673	0.8691	0.2	450.82	10.12	0.8718	0.5	
0.96	0.4	0.8149	0.8181	0.4	450.82	13.50	0.8221	0.9	
0.96	0.5	0.7573	0.7637	0.8	450.82	16.87	0.7669	1.2	
0.96	0.6	0.6940	0.7025	1.2	450.82	20.24	0.703	1.3	
0.96	0.7	0.6238	0.6153	1.4	450.82	23.62	0.623	0.1	two phase
0.96	0.75	0.5857	2-phase		450.82	25.31	0.5699	2.8	two phase
0.96	0.8	0.5456	2-phase		450.82	26.99	0.4879	11.8	two phase
0.98	0.2	0.9223	0.9219	0.0	460.21	6.75	0.9232	0.1	
0.98	0.3	0.8788	0.8789	0.0	460.21	10.12	0.8814	0.3	
0.98	0.4	0.8316	0.8325	0.1	460.21	13.50	0.8363	0.6	
0.98	0.5	0.7802	0.7825	0.3	460.21	16.87	0.7879	1.0	
0.98	0.6	0.7242	0.7290	0.7	460.21	20.24	0.7321	1.1	
0.98	0.7	0.6627	0.6685	0.9	460.21	23.62	0.6676	0.7	
0.98	0.75	0.6297	0.6274	0.4	460.21	25.31	0.6296	0.0	
0.98	0.8	0.5950	0.5774	3.0	460.21	26.99	0.5851	1.7	
1	0.2	0.9286	0.9279	0.1	469.60	6.75	0.9286	0.0	
1	0.3	0.8890	0.890	0.1	469.60	10.12	0.8901	0.1	
1	0.4	0.8463	0.847	0.1	469.60	13.50	0.849	0.3	
1	0.5	0.8002	0.804	0.4	469.60	16.87	0.8049	0.6	
1	0.6	0.7503	0.7565	0.8	469.60	20.24	0.7566	0.8	
1	0.7	0.6960	0.703	1.0	469.60	23.62	0.7022	0.9	
1	0.8	0.6369	0.6370	0.0	469.60	26.99	0.6388	0.3	
1	0.85	0.6052	0.5921	2.2	469.60	28.68	0.6011	0.7	
1	0.9	0.5720	0.5274	8.5	469.60	30.37	0.5566	2.8	
1.1	0.2	0.9519	0.9510	0.1	516.56	6.75	0.9497	0.2	
1.1	0.4	0.8989	0.896	0.3	516.56	13.50	0.897	0.2	
1.1	0.6	0.8403	0.836	0.5	516.56	20.24	0.8406	0.0	
1.1	0.8	0.7751	0.775	0.0	516.56	26.99	0.7804	0.7	
1.1	1	0.7021	0.7010	0.2	516.56	33.74	0.7157	1.9	
1.1	1.2	0.6199	0.6219	0.3	516.56	40.49	0.6462	4.1	
1.1	1.4	0.5266	0.5375	2.0	516.56	47.24	0.5752	8.5	
1.2	0.2	0.9662	0.9640	0.2	563.52	6.75	0.9641	0.2	
1.2	0.3	0.9485			563.52	10.12	0.946	0.3	
1.2	0.4	0.9301	0.9260	0.4	563.52	13.50	0.927	0.3	
1.2	0.6	0.8913	0.8840	0.8	563.52	20.24	0.8906	0.1	
1.2	0.8	0.8496	0.8430	0.8	563.52	26.99	0.8531	0.4	
1.2	0.9	0.8276			563.52	30.37	0.8343	0.8	
1.2	1	0.8047	0.7960	1.1	563.52	33.74	0.8156	1.3	
1.2	1.2	0.7561	0.749	0.9	563.52	40.49	0.778	2.8	
1.2	1.4	0.7034	0.7046	0.2	563.52	47.24	0.7429	5.3	
1.2	1.6	0.6460	0.6545	1.3	563.52	53.98	0.7099	9.0	
1.3	0.2	0.9755	0.974	0.2	610.48	6.75	0.9743	0.1	
1.3	0.4	0.9498	0.9446	0.5	610.48	13.50	0.9488	0.1	
1.3	0.6	0.9227	0.9158	0.8	610.48	20.24	0.9236	0.1	
1.3	0.8	0.8943	0.8893	0.6	610.48	26.99	0.8989	0.5	
1.3	1	0.8642	0.8556	1.0	610.48	33.74	0.8749	1.2	
1.3	1.2	0.8325	0.8257	0.8	610.48	40.49	0.852	2.3	
1.3	1.4	0.7990	0.7961	0.4	610.48	47.24	0.8304	3.8	
1.3	1.6	0.7635	0.7667	0.4	610.48	53.98	0.8107	5.8	
1.3	1.8	0.7258	0.7377	1.6	610.48	60.73	0.7930	8.5	
1.3	2	0.6858	0.7136	3.9	610.48	67.48	0.7779	11.8	

1.4	0.2	0.9818	0.981	0.1	657.44	6.75	0.9817	0.0
1.4	0.4	0.9629	0.9609	0.2	657.44	13.50	0.9638	0.1
1.4	0.6	0.9433	0.9405	0.3	657.44	20.24	0.9466	0.4
1.4	0.8	0.9229	0.9198	0.3	657.44	26.99	0.93	0.8
1.4	1	0.9017	0.8975	0.5	657.44	33.74	0.9143	1.4
1.4	1.2	0.8797	0.8754	0.5	657.44	40.49	0.8996	2.2
1.4	1.4	0.8568	0.8557	0.1	657.44	47.24	0.886	3.3
1.4	1.6	0.8329	0.8366	0.4	657.44	53.98	0.8737	4.7
1.4	1.8	0.8080	0.818	1.2	657.44	60.73	0.8627	6.3
1.4	2	0.7820	0.8038	2.7	657.44	67.48	0.8533	8.4
1.4	2.5	0.7118	0.7703	7.6	657.44	84.35	0.8372	15.0
1.6	0.2	0.9893	0.9887	0.1	751.36	6.75	0.9912	0.2
1.6	0.4	0.9783	0.9783	0.0	751.36	13.50	0.983	0.5
1.6	0.6	0.9671	0.9685	0.1	751.36	20.24	0.9754	0.9
1.6	0.8	0.9556	0.9598	0.4	751.36	26.99	0.9683	1.3
1.6	1	0.9439	0.9483	0.5	751.36	33.74	0.9619	1.9
1.6	1.2	0.9319	0.9355	0.4	751.36	40.49	0.9562	2.5
1.6	1.4	0.9196	0.924	0.5	751.36	47.24	0.9512	3.3
1.6	1.6	0.9071	0.913	0.6	751.36	53.98	0.947	4.2
1.6	1.8	0.8942	0.900	0.6	751.36	60.73	0.9435	5.2
1.6	2	0.8811	0.8884	0.8	751.36	67.48	0.9408	6.3
1.6	2.5	0.8468	0.8672	2.3	751.36	84.35	0.9374	9.7
1.6	3	0.8104	0.8538	5.1	751.36	101.22	0.9388	13.7
1.8	0.2	0.9932	0.991	0.2	845.28	6.75	0.9967	0.3
1.8	0.4	0.9864	0.9858	0.1	845.28	13.50	0.9939	0.8
1.8	0.6	0.9795	0.9823	0.3	845.28	20.24	0.9915	1.2
1.8	0.8	0.9724	0.9783	0.6	845.28	26.99	0.9895	1.7
1.8	1	0.9653	0.974	0.9	845.28	33.74	0.988	2.3
1.8	1.2	0.9581	0.9651	0.7	845.28	40.49	0.9869	2.9
1.8	1.4	0.9507	0.957	0.7	845.28	47.24	0.9862	3.6
1.8	1.6	0.9433	0.9509	0.8	845.28	53.98	0.9861	4.3
1.8	1.8	0.9357	0.9455	1.0	845.28	60.73	0.9863	5.1
1.8	2	0.9281	0.9393	1.2	845.28	67.48	0.9871	6.0
1.8	2.5	0.9085	0.9269	2.0	845.28	84.35	0.9908	8.3
1.8	3	0.8881	0.9291	4.4	845.28	101.22	0.9971	10.9

Note: The Z values obtained from a Soave-Redlich-Kong EOS program calculation for high $Tr > 1.1$ and $Pr > 1$ seem to show systematic too high values. For instance at $Tr = 1.8$ and $Pr > 1.2$ the values slightly dip and then rise again barely getting below 0.99 !! The Lydersen Chart for the isotherm $Tr=1.80$ shows a minimum value of about 0.92 however this occurs at a reduced pressure value of close to $Pr = 4$ (and not at about $Pr = 1.5$ as the Z-srk values show here).

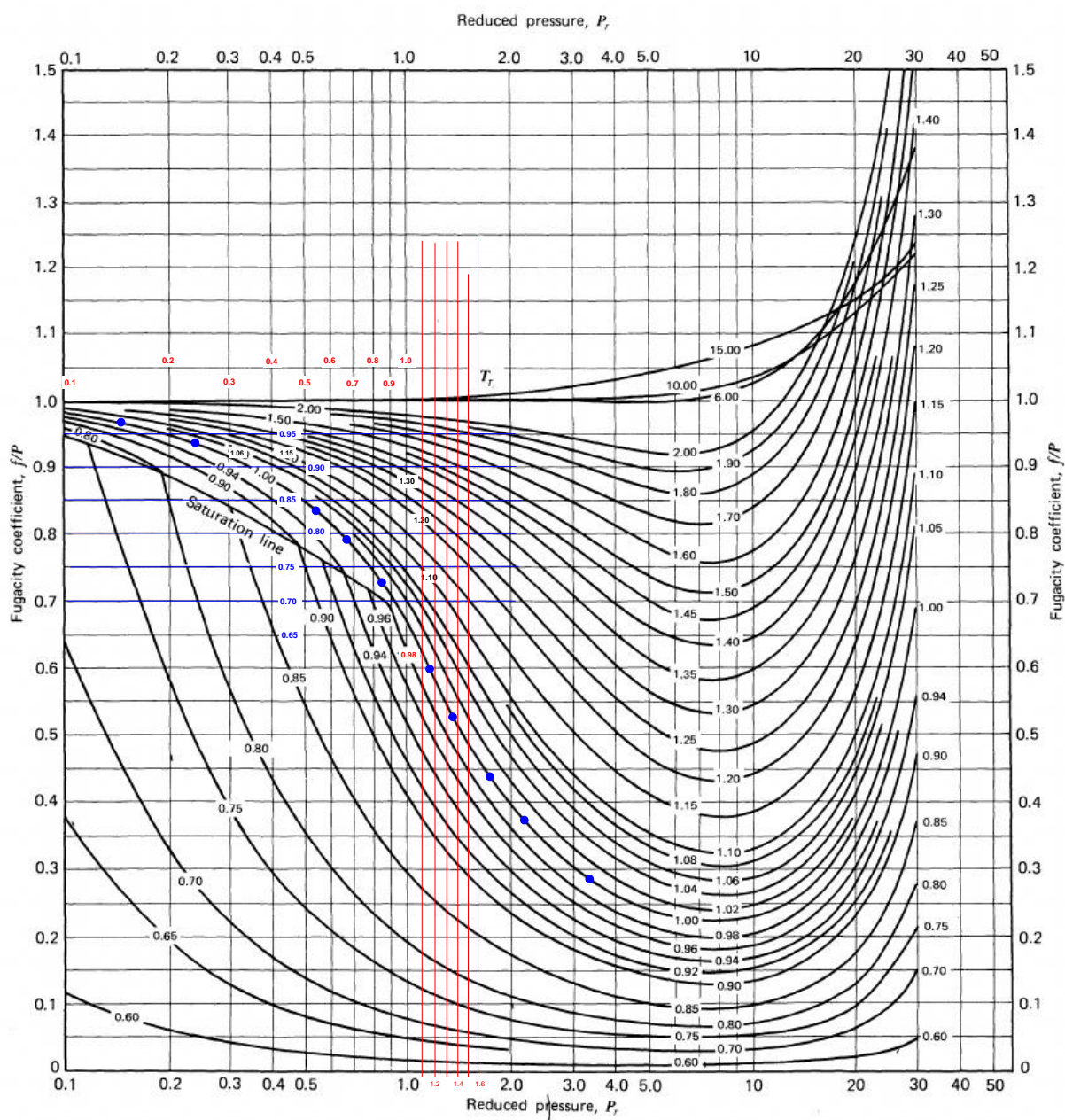
==Next Page contains a marked up copy of the Hougen – Ragatz Chart ==

Appendix - B The Hougen- Ragatz Chart

APPENDIX

B

Generalized Fugacity Coefficients of Pure Gases and Liquids ($Z_c = 0.27$)



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