Third Virial Coefficients

Silicon Valley FIG

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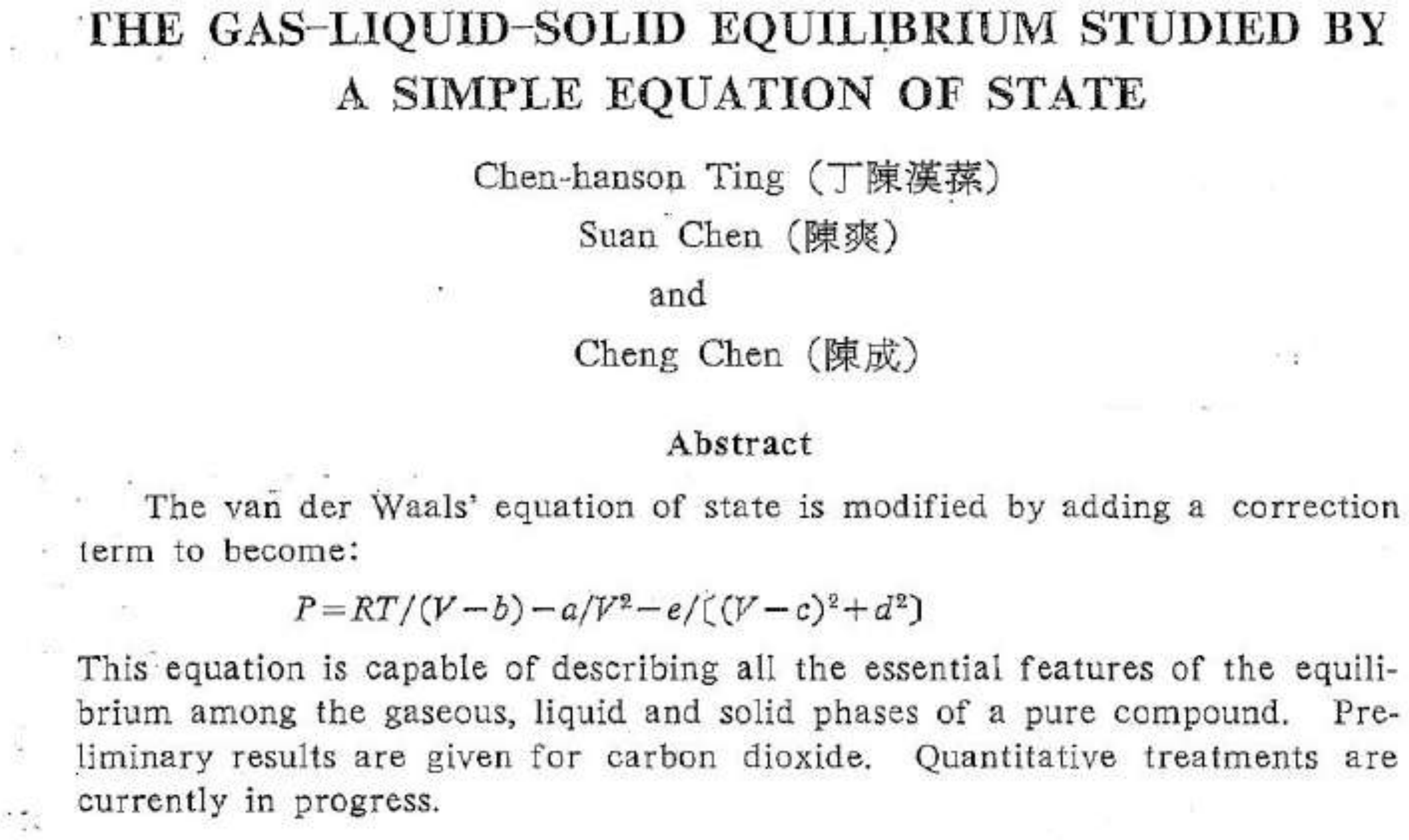
Summary

- Gas-Liquid-Solid Equilibrium
- 2nd and 3rd Virial coefficient
- Van der Waals, 1873
- Virial Equation of state, 1906
- Beattie–Bridgeman, 1928
- Benedict-Webb-Rubin, 1940
- Starling-Hans, 1972
- Lee-Kesler, 1975
- Cubic Virial Equation, 2017

Original Paper in 1972



THE GAS–LIQUID–SOLID EQUILIBRIUM STUDIED BY A SIMPLE EQUATION OF STATE

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Abstract

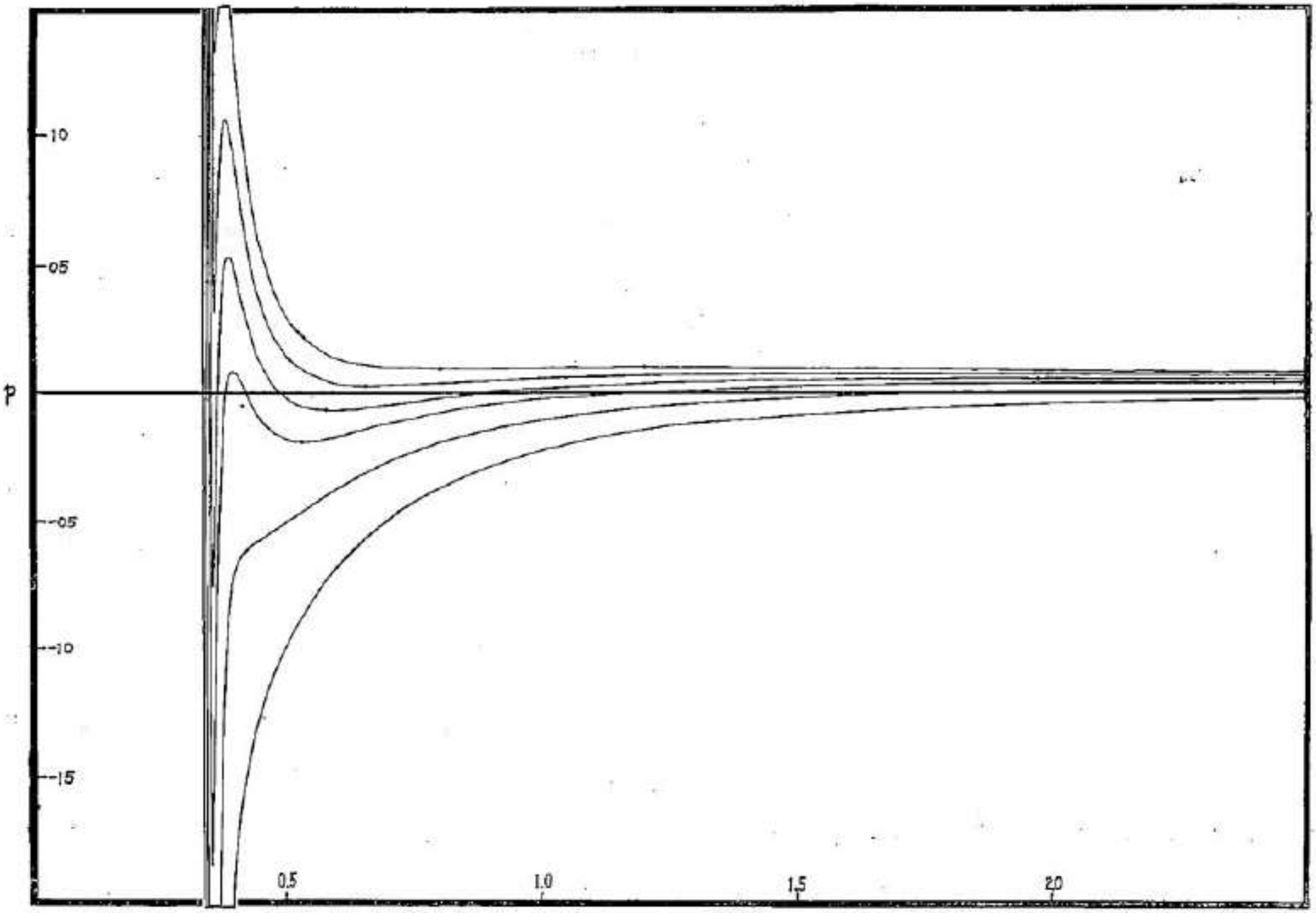
The van der Waals' equation of state is modified by adding a correction term to become:

$$P = RT/(V-b) - a/V^2 - e/[(V-c)^2 + d^2]$$

This equation is capable of describing all the essential features of the equilibrium among the gaseous, liquid and solid phases of a pure compound. Preliminary results are given for carbon dioxide. Quantitative treatments are currently in progress.

A Desktop Wang Computer

Plot on Wang Computer



Gas-Liquid-Solid Phases

The best virial EOS is with n=26:

$$p = 3t/v - 3(1- v_s/v)(1-(v_m/v)^{26})(1-(v_l/v)^{26})/v^2$$

For Argon at the triple point,

$t=0.553$

$p=0.0142$

$v_s=0.330$

$v_l=0.378$

$v_m=0.354$

$n=26$

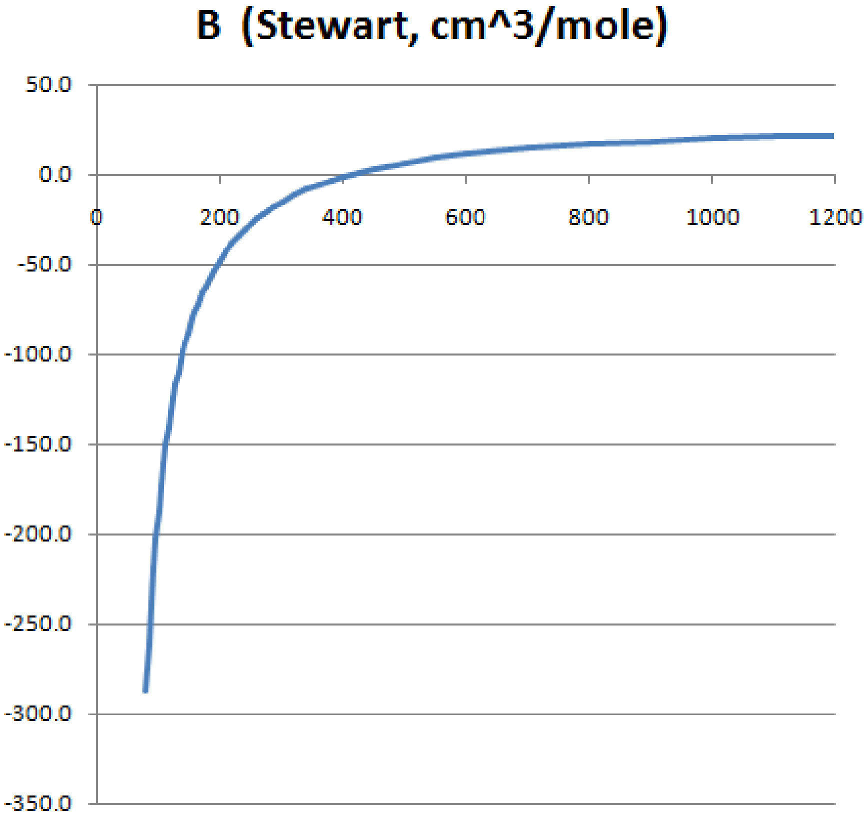
2^{nd} and 3^{rd} Virial Coefficients

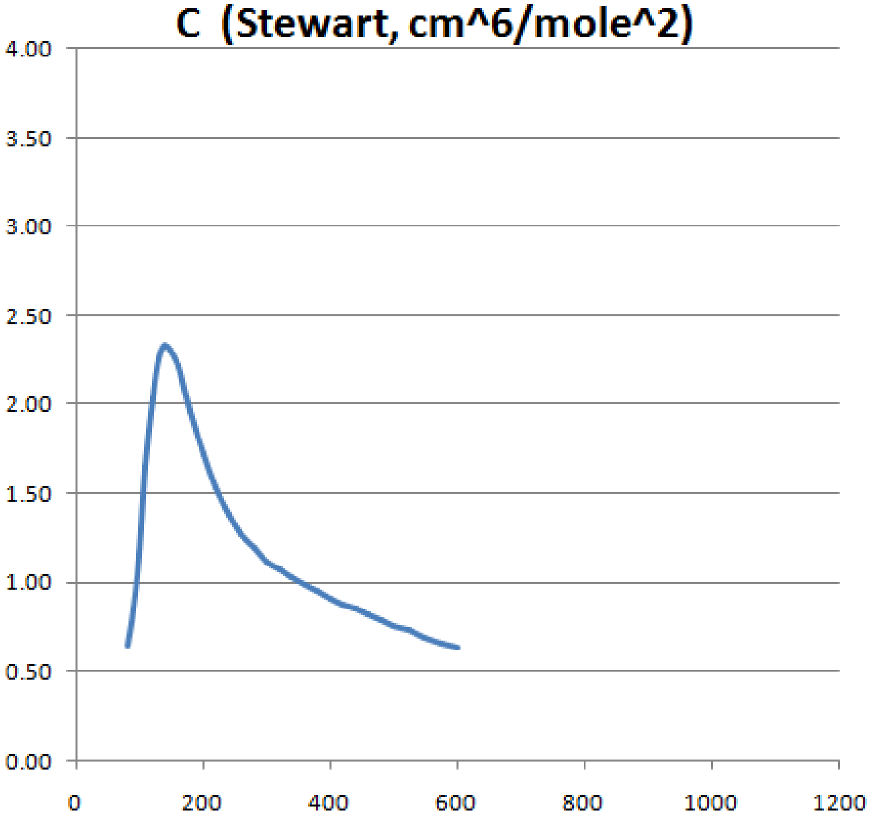
The 2^{nd} and 3^{RD} virial coefficients had been studied for more than 100 years.

All existing studies showed that they are not correlated.

Argon has been a typical gas for extensive experimental studies.

2nd and 3rd Virial coefficients of Argon


B (Stewart, cm^3/mole)


C (Stewart, cm^6/mole^2)

Virial Equation of State

Compressibility Z as a function of density ρ and temperature T:

$$Z = P/RT\rho = (1 + B\rho + C\rho^2 + D\rho^3 + E\rho^4 + F\rho^5 + G\rho^6 + \ldots)$$

Virial coefficients B-G… depend only on temperature.

Van der Waals, 1873

$$P=RT/(v-b) + a/v^2$$

It can be recast in virial form:

$$Z=1+(b-a/RT)/v+b^2/v^2+b^3/v^3+b^4/v^4+ \dots$$

Third virial coefficient is a constant b^2.

Beattie–Bridgeman, 1928

$$P=RT\,(1-c/vT^3)(v+B)\,/v^2-A/v^2$$

$$A=A_0(1-a/v)$$

$$B=B_0(1-b/v)$$

$$Z=1+(B_0-A_0/RT-c/T^3)/v$$

$$-(B_0b-A_0a/RT+B_0c/T^3)/v^2+B_0bc/T^3v^3$$

The third virial coefficient is negative.

Benedict-Webb-Rubin, 1940

$$P= RT\rho+(B_0RT-A_0-C_0/T^2)\rho+(bRT-a/T)\rho^2$$

$$+a\alpha\rho^5+(c/T^2)(1+\gamma\rho^2)(\exp(-\gamma\rho^2))\rho^3$$

$$Z=1+(B_0-A_0/RT-C0/RT^3)\ \rho$$

$$+(b-a/RT)\ \rho^2$$

$$+(a\alpha/RT)\rho^5+(c/RT^3)(1+\gamma\rho^2)(\exp(-\gamma\rho^2))\ \rho^3$$

The exponential term is troublesome.

Benedict-Webb-Rubin, 1940

The exponential term is rapidly converging, and can be expanded:

$$\exp(-\gamma\rho^2)=1-\gamma\rho^2$$

Then, it has a much simpler virial form:

$$Z=1+(B_0-A_0/RT-C0/RT^3)\ \rho$$
$$+(b-a/RT+\ c/RT^3)\ \rho^2$$
$$+(a\alpha/RT)\rho^5-(c/RT^3)\gamma^2\rho^6$$

Starling-Hans, 1972

$$P=RT\rho+(B_0RT-A_0-C_0/T^2+D_0/T^3-E_0/T^4)\rho$$
$$+(bRT-a+d/T)\rho^2$$
$$+\alpha(a+d/T)\rho^5+(c/T^2)(1+\gamma\rho^2)(\exp(-\gamma\rho^2))\rho^3$$

Then, it has a virial form:

$$Z=1+(B_0-A_0/RT-C_0/RT^3+D_0/RT^4-E_0/RT^5)\rho$$
$$+(b-a/RT-d/RT^2+ c/RT^3)\rho^2+$$
$$\alpha(a/RT+d/RT^2)\rho^5+(c/RT^3)\gamma^2\rho^6$$

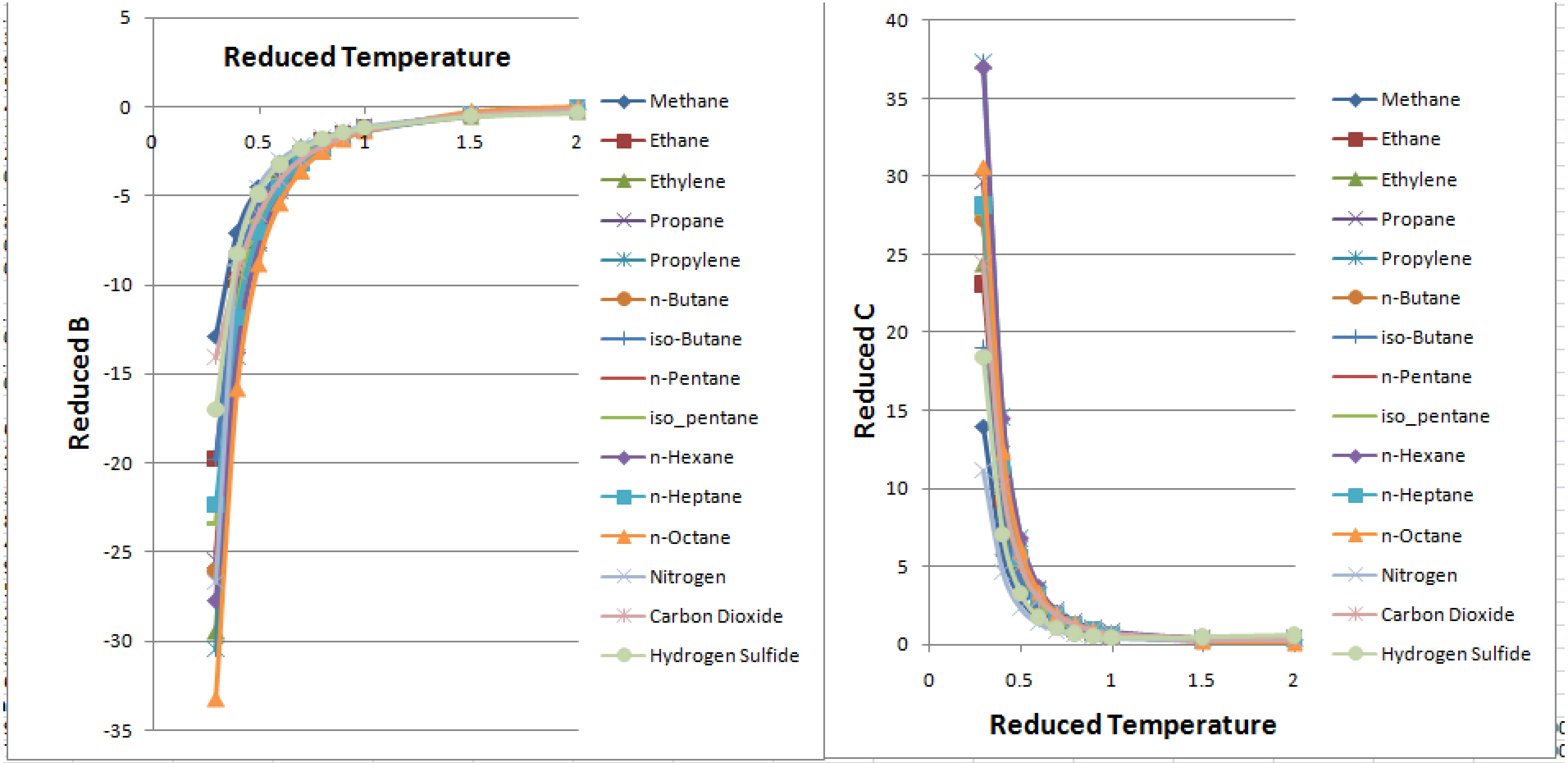
Lee-Kesler, 1975

A single equation generalized for many different compounds:

$$Z=1+(b_1-b_2/t-b_3/t^2-b_4/t^3)\rho$$
$$+(c_1-c_2/t+c_3/t^3)\rho^2$$
$$+(d_1+d_2/t)\rho^5+(c_4/t^3)(\beta+\gamma\rho^2)(\exp(-\gamma\rho^2))\rho^3$$

$t=T/T_c$ and $\rho=RT_c/P_cV$

Starling-Hans, 1972



Cubic Virial Equation

A virial EOS truncated to the third term

$$P = (RT/v)(1+B/v+C/v^2)$$

It has all the nice properties of van der Waals EOS, but without the singular point.

$$P=RT/(v-b)+a/v^2$$

Cubic Virial Equation

At the critical point, assuming:

$dP/dv=0$; and $d^2P/dv^2=0$

Cubic virial equation can be solved to get: $B=-v_c$; $C=v_c/3$ and $Z_c=0.333$

Z_c is better than what van der Waals results, 0.375, but still not close to actual values , 0.26-0.30.

Cubic Virial Equation

Cubic virial equation dominates the virial equation of state, and should be studied more carefully and more thoroughly.

The second and third virial coefficients in the reduced forms still show divergent behavior, and need more studies.

Cubic Virial Equation

Virial equations were generally constructed with ‘multiproperty analysis’ or ‘multivariable regression’, and you don’t know what happened underneath.

Now, cubic virial equation can be constructed first using ‘second order regression’ to obtain 2nd and 3rd coefficients. Residues can be analyzed separately.

Cubic Virial Equation

Using cubic virial equation, 2nd and 3rd coefficients can be solved analytically in the saturation region. They should be used to check results from second order regressing.

Residues from higher virial coefficients must be analyzed after 2nd and 3rd coefficients are determined precisely.

Conclusions

Properly determined 3rd virial coefficients will reduce complexity in virial EOS, and improve its accuracy.

My cubic virial EOS has great value in improving our understanding of real gases, particularly in the saturation region.

Questions?

Thank You Very Much!