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Determination of limit of stability of chemical systems

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Abstract

This work presents a new statement of the stability criteria for pure substances described by Peng-Robinson equation of state. A method for solving the limit of stability of chemical systems has been developed, based on the use of Newton – Raphson's method of convergence for finding the roots of equation. The method provides a thermodynamically rigorous method for predicting the limit of stability of pure substances. This method can also be used for multi-component mixtures, provided that a different stability criterion is assumed. Application was made to Benzene. At 522K, the limit of stability of liquid and vapour Benzene were 10 bar and 35 bar respectively. Peng - Robinson equation of state was found to be adequate in predicting the limit of stability of both liquid and vapour phases of benzene.

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1. Introduction

One useful area of application of thermodynamics is in predicting the stability of systems. The focus of this work is on the stability of chemical systems. The work is limited to two phase systems of pure materials. Normally, the criterion for the co-existence of phases in equilibrium is well known. These are the equality of temperatures, pressures and component chemical potentials in all the phases. These criteria are valid even if chemical reactions occur in one or more of the phases. They are useful in predicting phase behaviour in equilibrium. However, in some applications, there is need to understand the behaviour of phases that are not only in equilibrium but are stable. The stability referred to here is with respect to minor perturbations. In the special cases of super heated liquids and subcooled vapours, evaporation and condensation are suppressed beyond their normal operating temperatures and pressures. Although, these thermodynamic states are stable, there exist several metastable states in the envelop covering the region of saturated liquid and vapour. The stable states themselves cannot remain stable beyond certain operating variables where spontaneous evaporation or condensation must occur. These are the limits of stability.

The stability of pure substances is important from both a theoretical and practical point of view, and an ability to predict this condition is highly desirable. Use of the thermodynamic criterion together with a single 2-parameter equation of state has yielded results which are remarkably reliable and easy to obtain (Peng and Robinson,1976).

Various equations of state are widely used to correlate stability limit in single component systems. Stability computation procedures are generally poorly behaved in the vicinity of the critical point and convergence is achieved in this region, if at all, at considerable cost in computational effort. No one equation is sufficiently accurate to represent all real gases under all conditions (Sinnott, 1999). The modern development of cubic equations of state was initiated in 1949 by publication of the Redlich/Kwong (RK) equation (Redlich et al, 1949). The simplest expressions that (in principle) represent both the vapour and liquid phase volumetric behaviour of pure fluids are equations cubic in molar volume. For a range of lower pressures, there are three (3) real positive roots. Here, the middle root is of no significance, the smallest root is a liquid or liquid like volume and the largest root is a vapour or vapour like volume (Smith et al, 2001 and Perry et al, 1999). Peng – Robinson equation is related to the Redlich-Kwong Soave equation of state and was developed to overcome the instability in the Redlich-Kwong-Soave equation near the critical point (Peng and Robinson, 1977). Benzene is a volatile, colourless, and flammable liquid aromatic hydrocarbon which possesses a characteristic odour (Kirk and Othmer, 1978). Benzene is by far the most important aromatic petrochemical raw material (Kent, 1992).

2. Model development

2.1. Evaluating the limits of stability

2.1.1. Application of equation of state

Using Peng – Robinson equation of state

$$P = \frac{RT}{V - b} - \frac{a(w, T_r)}{V(V + b) + b(V - b)} \qquad (1)$$

$a(w, T_r) = a(Tc)\ \alpha\ (w, T_r)$

$$a(T_c) = \frac{0.45724R^2\ T_c^{\ 2}}{P_c}$$

$\alpha(w,T_C) = [\ (1+K\ (1- T_r^{1/2})\ ]^2$

$K = 0.37464 + 1.5422w - 0.2699w^2$

$$b = \frac{0.7780RT_c}{P_c}$$

At the limit of stability, Avv = 0 is the most convenient That is

$$Avv = \left(\frac{\partial P}{\partial V}\right)_{T,N} = 0 \qquad (2)$$

With N constant. Differentiating equation (1) with respect to V at constant temperature,

$$\left(\frac{\partial P}{\partial V}\right)_T = 0 = \frac{-RT}{(V - b)^2} + \frac{2a(w,T_r)(V + b)}{[V(V + b) + b(V - b)]^2} \qquad (3)$$

Rearranging equation (3),

$$\frac{RT}{(V - b)^2} = \frac{2a(w, T_r)\,(V + b)}{[(V(V + b) + b(V - b)]^2}$$

$$T = \frac{2a(w, T_r)\,(V + b)\,(V - b)^2}{R[V(V + b) + b(V - b)]^2} \qquad (4)$$

Let $A(w,T_r)$ be represented by A and b be represented by B, Substituting equation (4) into equation (1) gives

$$P = \frac{R(2A)(V + B)(V - B)^2}{R[V(V + B) + B(V - B)]^2\,(V - B)} - \frac{A}{V(V + B) + B(V - B)}$$

Simplifying above equation gives

$$P = \frac{AV^2 - 2ABV - AB^2}{V^4 + 4BV^3 + 2B^2V^2 - 4B^3V + B^4}$$

Cross multiplying and rearranging gives

$PV^4 + 4PBV^3 + (2PB^2 – A)\ V^2 + (2AB-4PB^3)V + PB^4 + AB^2 = 0$ (5)

To get T – Isotherm from Peng-Robinson equation of state, consider equation (1.1)

$$P = \frac{RT}{V - b} - \frac{a(a, T_r)}{V(V + b) + b(V - b)}$$

Which implies that

$$P = \frac{RT}{V - B} - \frac{A}{V(V + B) + B(V - B)}$$

$$P = \frac{RT\,(V + B) + B(V - B)] - A(V - B)}{(V - B)\,(V^2 + 2BV - B^2)}$$

Let RT be represented by C

$$\therefore P = \frac{C(V^2 + 2BV - B^2) - A(V - B)}{V^3 + 2BV^2 - B^2V - BV^2 - 2B^2V - B^3}$$

$$P = \frac{CV^2 + 2CBV - CB^2 - AV + AB}{V^3 + BV^2 - 3B^2V - B^3}$$

Cross multiplying and rearranging

$PV^3+(PB-C)V^2+(A-3PB^2-2CB)V+CB^2-PB^3-A=0$ (6)

2.1.2. Method of computation

Application was made to Benzene at 420K, 467K and 522K. Plotting P against V, the curve of limit of stability is obtained. From equation (5)

$$\text{Let} \begin{pmatrix} E = 4PB \\ F = 2PB^2 - A \\ G = 2AB - 4PB^3 \\ H = PB^4 + AB^2 \end{pmatrix} \qquad (7)$$

Substituting equation (7) into equation (5) gives

$PV^4+EV^3+FV^2+GV+H = 0$ (8)

Taking the first derivative of equation (2.8) gives

$F'(V) = DV = 4PV^3+3EV^2+2FV+G$

The roots (volumes) of equation (8) were found using Newton – Raphson's method of convergence. The values of A and B change with temperature and substance.

Also, considering equation (6)

$PV^3+(PB-C)V^2+(A-3PB^2-2CB)V+CB^2-PB^3-AB = 0$

$$\text{Let} \begin{pmatrix} E = PB - C \\ F = A - 3PB^2 - 2CB \\ G = CB^2 - PB^3 - AB \end{pmatrix} \quad (9)$$

Substituting equation (9) into equation (6) gives

$$PV^3+EV^2+FV+G = 0 \quad (10)$$

Taking the first derivative of equation (10) gives

$$F'(V) = DV = 3PV^2 + 2EV + F \quad (11)$$

Equations (6) and (10) were solved for benzene and the roots (volumes) at different pressures for a fixed temperature were obtained.

3. Results and discussion

A method was developed, based on the use of Newton – Raphson's method of convergence for finding the roots of equation. Application was made to Benzene at three different temperatures (420K, 467K and 522K).

Equations (6) and (10) were solved separately for Benzene and the roots (volumes) for a fixed temperature and at different pressures were obtained. From equation (6), the plot of pressure against volume gave the limit of stability curve. Equation (10), gave the T-isotherm. Where the two plots cut each other gave the limit of stability. This point gave the volume and pressure at the limit of stability for a given temperature. The results are given in Tables 1-12 and Figs. 1-6.

From Figs. 1 and 2, it is seen that 420K, the liquid phase benzene is unstable. This is because 420K is well below the critical temperature. For this temperature, the volume was constant, no matter the pressure. At 420K, and for vapour phase, the limit of stability of benzene was 17 bar.

At 467K, and for liquid phase, benzene was unstable Fig. 3. Again, this is because 467K is below the critical temperature. At 467K and for vapour phase, benzene is stable and the limit of stability was 24 bar Fig.4. At this temperature, the limit of stability increased as the critical temperature increased.

At 522K, the limit of stability of liquid benzene was 10 bar while the limit of stability of vapour phase was 35 bar Figs. 5 and 6. Figures 1 and 3 showed that T-isotherm for benzene is straight lines perpendicular to volume axis. This means that volume was constant irrespective of pressure. This can be explained by the fact that at these temperatures, the Peng-Robinson equation of state does not describe the liquid phase of benzene. The limit of stability lines from these figures are slightly curved, tending to straight lines. For this case, the stability criterion equation did not very well describe the liquid phase at the given temperatures.

4. Conclusion

Peng – Robinson equation of state has been found to be adequate in predicting the limit of stability of both liquid and vapour phase of pure substances. The method developed is expected to be equally applicable to other pressure – explicit equation of state. Though application has been made to benzene, it is hoped that the method will apply to other chemical systems. This method can also be used for multicomponent mixtures, provided that a different stability criterion is assumed.

References

Kent, J. A., 1992. Riegel's Handbook of Industrial Chemistry. 9th ed., Chapman and Hall Inc., New York, pp 849.

Kirk, R.E., Othmer, D.F., 1979. Encyclopedia of Chemical Technology, 3rd ed.. John Wiely Inc., New York.

Peng, D. Y., Robinson, D. B., 1976. A new two constant equation of state. Industrial Eng. Chem. Fundamentals, 15, 59, pp. 59 – 64.

Peng, D. Y., Robinson, D. B., 1977. A rigorous method of predicting the critical properties of multi-component systems for an equation of state. AICHE Journal, Vol. 23, No. 2, pp. 137.

Perry, R. H., Green, D. W., 1999. Chemical Engineers Handbook. 6th ed., McGraw Hill Coy. Inc., New York.

Redlich, O., Kwong, J. N., 1949. Chem. Rev., Vol. 44, pp. 233 – 244.

Sinnot, R. K., 1999. Chemical Engineering Design. In Coulson and Richardson's Chemical Engineering, Volume 6, 3rd ed., Elsevier Publishers, India pp. 340.

Smith, J. M., Van Ness, H. C., Abbot, M. M., 2001. Introduction to Chemical Engineering Thermodynamics. 6th ed., McGraw Hill publishers, pp. 93 – 98.

Appendix

Table 1
Estimated limit of stability for liquid benzene at 420K

Pressure, bar	Volume, m^3/mole x 10^4
1	1.805
2	1.8062
5	1.8238

10	1.8554
15	1.890
20	1.9283
25	1.9713
30	2.0203
35	2.0771
40	2.145
45	2.2295
48	2.2927

Table 2
T-Isotherm for liquid benzene at 420K

Pressure, bar	Volume, m^3/mole x 10^4
1	1.041
2	1.041
5	1.041
10	1.042
15	1.043
20	1.044
25	1.044
35	1.046
45	1.047

Table 3
Estimated limit of stability for vapour benzene at 420K

Pressure, bar	Volume, m^3/mole x 10^4
1	47.1343
2	32.6479
5	19.7706
10	13.2478
15	10.3326
20	8.5748
25	7.3509
30	6.4398
35	5.7076
40	5.0950
45	4.5508
48	4.2591

Table 4
T- Isotherm for vapour benzene at 420K

Pressure, bar	Volume, m^3/mole x 10^4
5	49.38
10	27.453
15	14.134
20	1.044
25	1.044
35	1.046
45	1.047

Table 5
Estimated limit of stability for liquid benzene at 467K

Pressure, bar	Volume, m^3/mole x 10^4
0	1.7949
3	1.8131
5	1.8257
10	1.8595
15	1.8968

Table 6:
T-Isotherm for liquid benzene at 467K

Pressure, bar	Volume, m^3/mole x 10^4
0	1.185
2	1.184
3	1.183
5	1.183
10	1.181
15	1.179
20	1.177
30	1.174
40	1.171

Table 7
Estimated limit of stability for vapour benzene at 467K

Pressure, bar	Volume, m^3/mole x10^4
3	25.3760
5	19.1124
10	12.7788
15	9.9456
20	8.2349
25	7.0472
30	6.1500
40	4.8217
45	4.2797
47	4.0715

Table 8
T-Isotherm for vapour benzene at 467K

Pressure, bar	Volume, m^3/mole x 10^4
15	19.645
20	12.312
30	1.174
40	1.171

Table 9
Estimated limit of liquid benzene at 522K

Pressure, bar	Volume, m^3/mole x 10^4
1	1.8013
2	1.8078
5	1.8280
10	1.8646
15	1.9053
20	1.9514
25	2.0043
30	2.0666
35	2.1424
40	2.2396
45	2.3776
48	2.5052

Table 10
T-Isotherm for liquid benzene at 522K

Pressure, bar	Volume, m^3/mole x 10^4
10	1.88
13	1.787
15	1.715
20	1.629
25	1.579
30	1.543
33	1.525
35	1.515
40	1.492
45	1.472

Table 11
Estimated limit of stability for vapour benzene at 522K

Pressure, bar	Volume, m^3/mole x 10^4
1	44.0412
2	30.4585
5	18.3808
10	12.2570
15	9.5146
20	7.8556
25	6.7006
30	5.82240
35	5.1147
40	4.5064
45	3.9447
48	3.5952

Table 12
T-Isotherm for vapour benzene at 522K

Pressure, bar	Volume, m^3/mole x 10^4
7	57.625
10	38.937
11	34.955
15	24.297
20	16.843
25	12.204
30	8.839
33	7.000
35	1.515
40	1.492
45	1.472

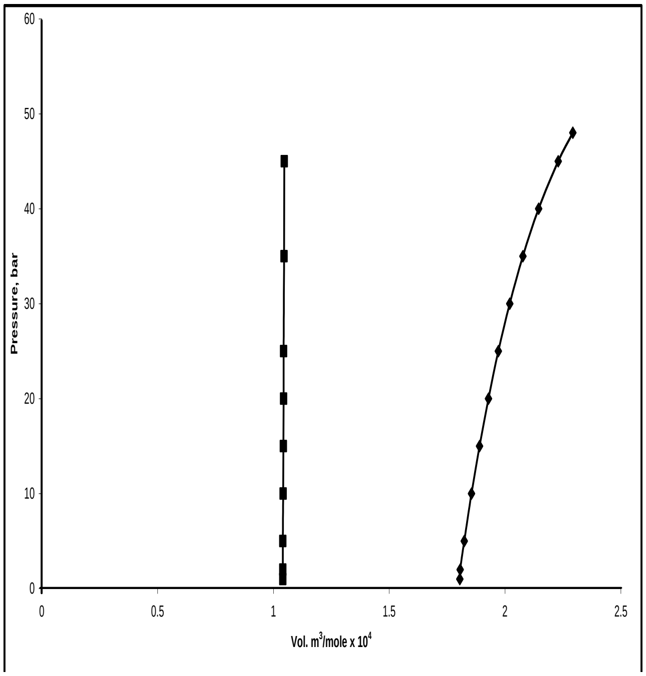

Fig. 1. Limit of Stability for Liquid Benzene at 420K

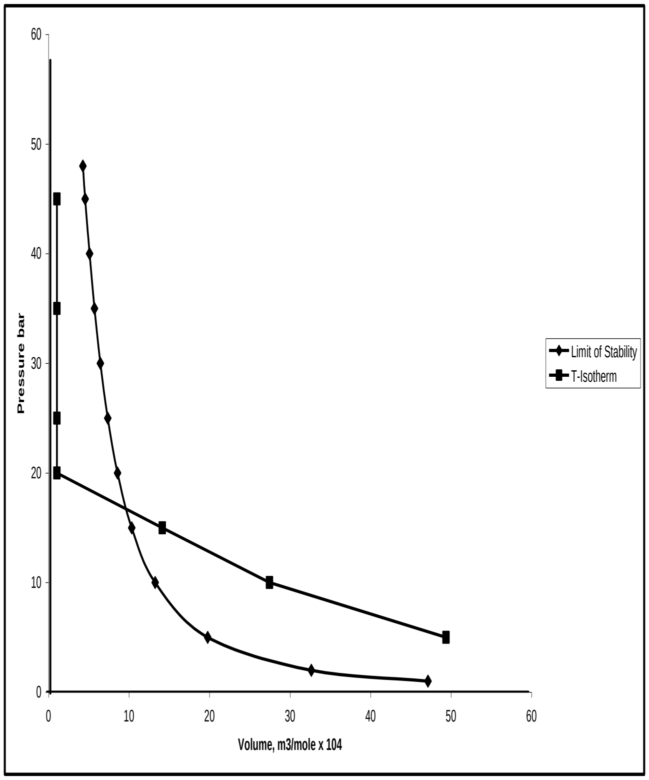

Fig. 2. Limit of stability for vapour benzene at 420K.

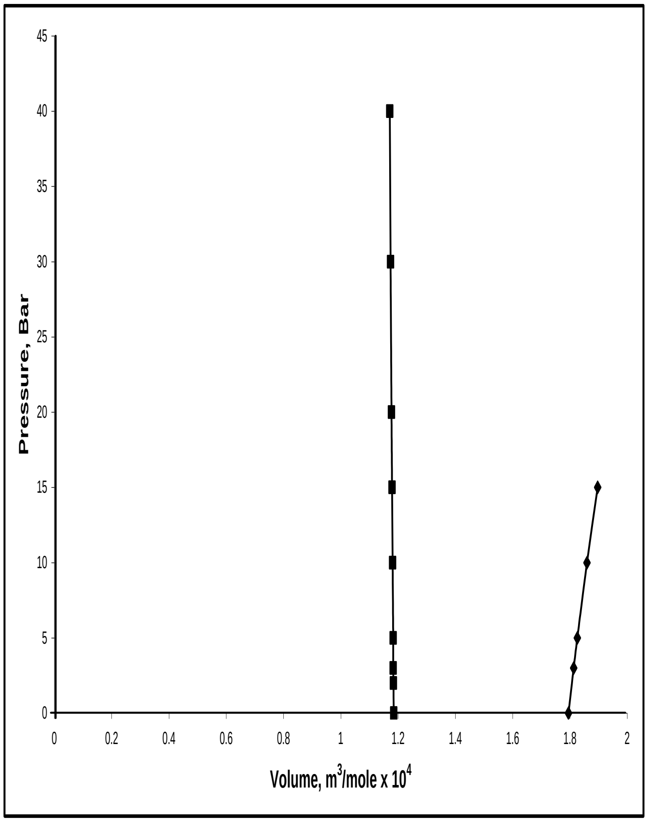

Fig. 3. Limit of stability for liquid benzene at 467K.

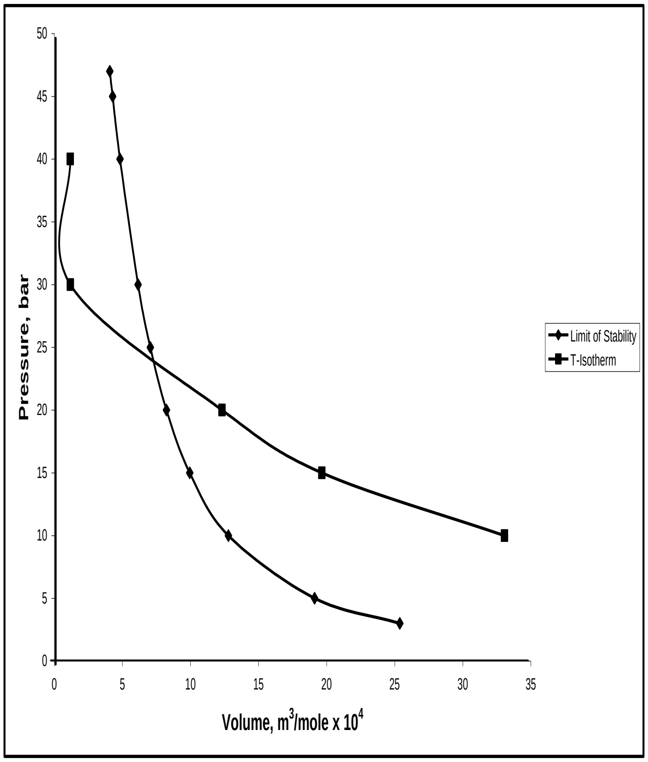

Fig. 4. Limit of stability for vapour benzene at 467K.

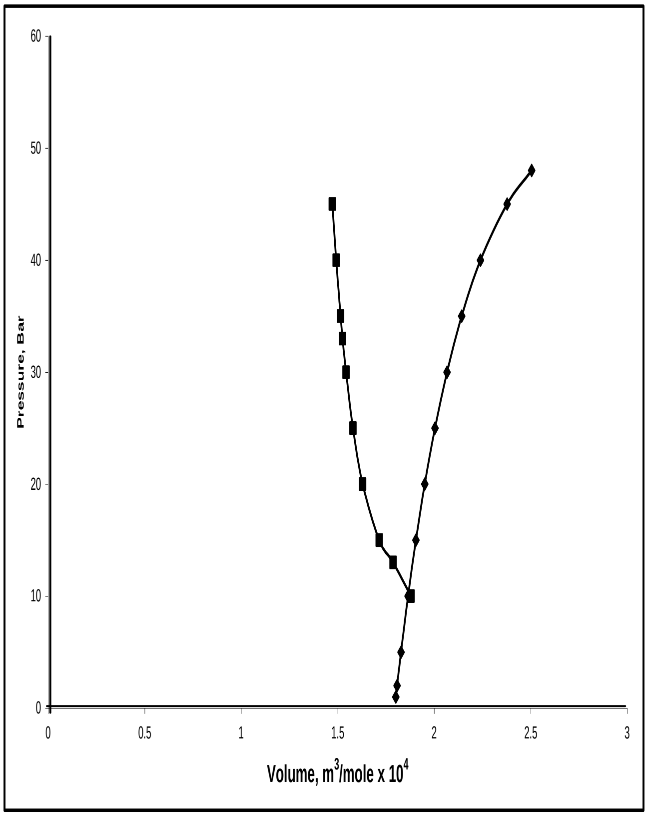

Fig. 5. Limit of stability for liquid benzene at 522K.

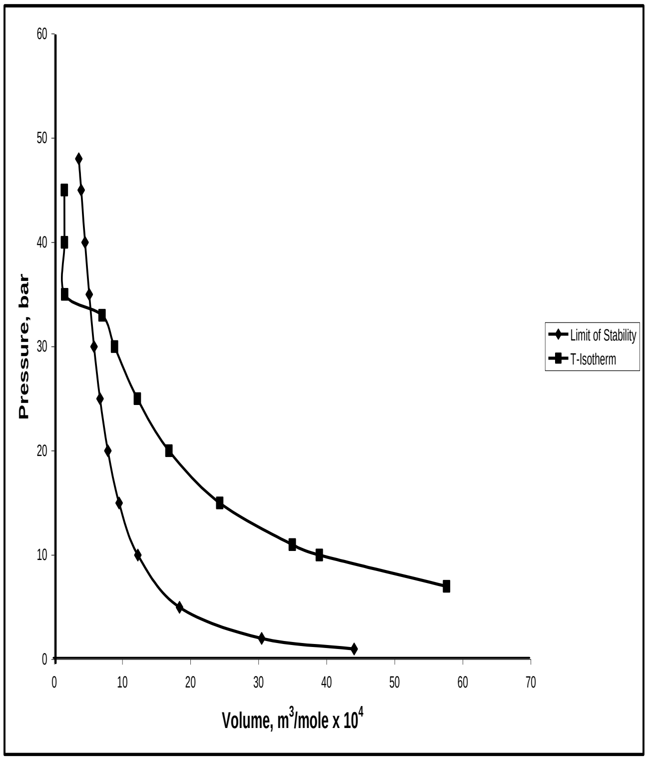

Fig. 6. Limit of stability for vapour benzene at 522K.