

# Liquid-Vapor Equilibrium Curves for Methane System by Using Peng-Robinson Equation of State

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## Abstract

This work presents liquid-vapour equilibrium curves for pure compounds, which is based on a computer program. For this purpose Peng-Robinson equation of state has been used for the measurement of equilibrium data. Equations system has solved by Using Newton-Raphson method, but at critical point this equations system are not converged and extrapolation technique is used. By using this program various equilibrium data such as saturated pressure and specific molar volume has been calculated and flowchart of this program and an applied example for methane system is presented in this article and conclusions are compared with experimental data and are shown by graphs and table.

**Key words** : modeling; equilibrium curve; Peng-Robinson equation of state; methane

## Introduction

Preparing of saturation curve for pure compounds by using equations of state is very important, especially for compounds that have not enough available information. In this article, using Peng-Robinson equation of state, equilibrium curves has been drew. In equilibrium calculations, equal's relation of fugacity in liquid and vapor phases is used and specific volumes of phases at equilibrium temperature are calculated by using a written program. Computer program flowchart is shown in Fig.1.

Finally, P-V and T-V diagrams for methane system are separately drew and conclusions were compared with experimental results.

## Calculations

In this calculations pure compounds saturation curve are presented by using Peng-Robinson equation of state. Versus equal pure compound's fugacity in vapor and liquid phases, specific volumes  $V_L$  and  $V_G$  are calculated at equilibrium temperature:

$$f^L = f(T, V_L) \quad (1)$$

$$f^G = f(T, V_G) \quad (2)$$

$$p^L = g(T, V_L) \quad (3)$$

$$p^G = g(T, V_G) \quad (4)$$

At equilibrium:

$$f^L = f^G \text{ and } p^L = p^G \quad (5)$$

$$f(T, V_L) = f(T, V_G) \quad (6)$$

$$g(T, V_L) = g(T, V_G) \quad (7)$$

Thus:

$$F(V_L, V_G) = 0 \quad (8)$$

$$G(V_L, V_G) = 0 \quad (9)$$

Therefore in a specified temperature, above two non-linear functions should be solved together. For solving this equations Newton-Raphson method is used. To assume that point  $(V_{Lo}, V_{Go})$  is the answer, 'f' and 'g' functions are expanded near it.

$$F(V_L, V_G) = F(V_{Lo}, V_{Go}) + F'_{VL}(V_{Lo}, V_{Go})(V_L - V_{Lo}) + F'_{VG}(V_{Lo}, V_{Go})(V_G - V_{Go}) \quad (10)$$

$$G(V_L, V_G) = G(V_{Lo}, V_{Go}) + G'_{VL}(V_{Lo}, V_{Go})(V_L - V_{Lo}) + G'_{VG}(V_{Lo}, V_{Go})(V_G - V_{Go}) \quad (11)$$

With combination of equations system (8), (9), (10) and (11):

$$V_L = V_{Lo} + D_{VL} \quad (12)$$

$$V_G = V_{Go} + D_{VG} \quad (13)$$

$$D_{VL} = [-F(V_{Lo}, V_{Go}) G'_{VG}(V_{Lo}, V_{Go}) + F'_{VG}(V_{Lo}, V_{Go}) G(V_{Lo}, V_{Go})] / \Delta \quad (14)$$

$$D_{VG} = [-F'_{VL}(V_{Lo}, V_{Go}) G(V_{Lo}, V_{Go}) + F(V_{Lo}, V_{Go}) G'_{VL}(V_{Lo}, V_{Go})] / \Delta \quad (15)$$

$$\Delta = \begin{vmatrix} F'_{VL}(V_{Lo}, V_{Go}) & F'_{VG}(V_{Lo}, V_{Go}) \\ G'_{VL}(V_{Lo}, V_{Go}) & G'_{VG}(V_{Lo}, V_{Go}) \end{vmatrix} \quad (16)$$

That  $\Delta$  is determinant.

Therefore in a specified saturation temperature ( $T^{\text{sat}}$ ),  $V_{Lo}$  and  $V_{Go}$  are guessed, then  $V_L$  and  $V_G$  are calculated from equations system (12) and (13). These calculations are repeated until  $V_L$  and  $V_G$  quantities in two-cascade iteration are equaled.

With these quantities at  $T^{\text{sat}}$ , equilibrium saturated pressure ( $P^{\text{sat}}$ ) is calculated by using Peng-Robinson equation of state. It should be noted that for calculations, initial quantities of  $V_{Lo}$  and  $V_{Go}$  at each temperature ( $T_i$ ) are the final quantities of  $V_L$  and  $V_G$  in last temperature ( $T_{i-1}$ ).

Now,  $F(V_L, V_G)$  and  $G(V_L, V_G)$  functions are obtained by using P-R equation of state:

$$\ln \Phi_{\text{pure}} = \frac{1}{RT} \int_v^{\infty} \left( \frac{P}{n} - \frac{RT}{V} \right) dV - RT \ln \frac{PV}{nRT} + RT \left( \frac{PV}{nRT} - 1 \right) \quad (17)$$

$$P = RT/(v-b) - a(T_C) \cdot \alpha(T_R, \omega) / (v^2 + 2vb - b^2) \quad (18)$$

$$b = 0.0778 RT_C / P_C \quad (19)$$

$$\beta = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \quad (20)$$

$$a(T_C) = 0.45727 R^2 T_C^2 / P_C \quad (21)$$

$$\alpha(T_R, \omega) = [1 + \beta(1 - T_R^{1/2})]^2 \quad (22)$$

Thus:

$$F(V_L, V_G) = -\frac{a \cdot \alpha}{2\sqrt{2} b RT} \ln \left\{ \frac{V_L + b(1 + \sqrt{2}) / [V_L + b(1 - \sqrt{2})]}{V_G + b(1 + \sqrt{2}) / [V_G + b(1 - \sqrt{2})]} \right\} + \ln \left\{ \frac{V_L / (V_L - b)}{V_G / (V_G - b)} \right\} + \dots$$

$$\left\{ \frac{V_L}{V_L - b} - \frac{V_G}{V_G - b} \right\} - \frac{a \cdot \alpha}{RT} \left\{ \frac{V_L}{V_L^2 + 2V_L b - b^2} - \frac{V_G}{V_G^2 + 2V_G b - b^2} \right\} - \dots$$

$$\ln \left\{ \frac{V_L / (V_L - b) - (a \cdot \alpha / RT) [V_L / (V_L^2 + 2V_L b - b^2)]}{V_G / (V_G - b) - (a \cdot \alpha / RT) [V_G / (V_G^2 + 2V_G b - b^2)]} \right\} = 0 \quad (23)$$

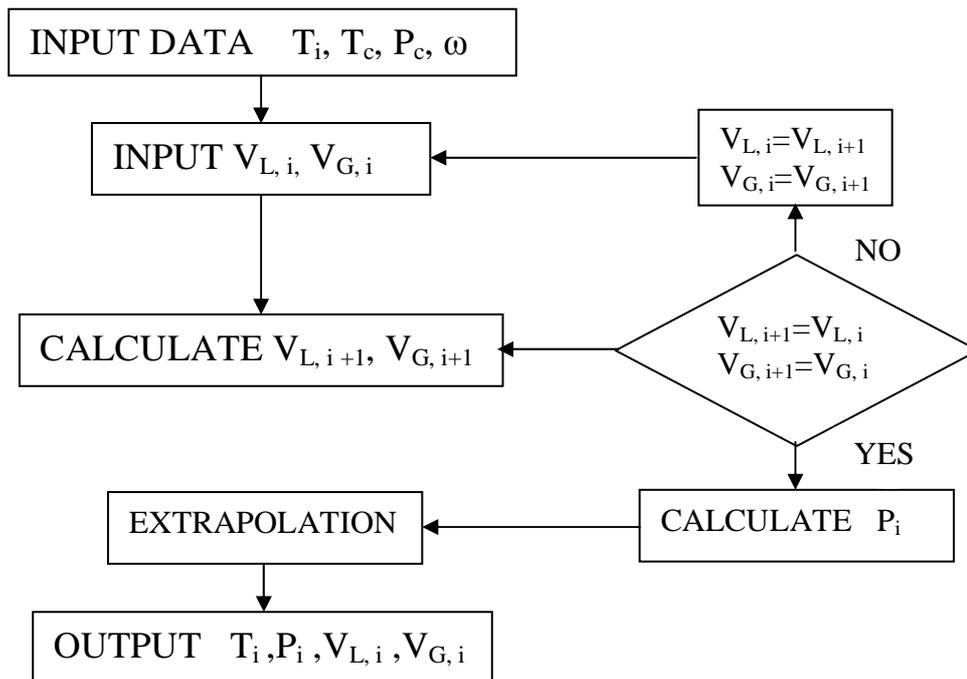
$$G(V_L, V_G) = \frac{1}{V_L - b} - \frac{1}{V_G - b} - \frac{a \cdot \alpha}{RT} \left\{ \frac{1}{V_L^2 + 2V_L b - b^2} - \frac{1}{V_G^2 + 2V_G b - b^2} \right\} = 0 \quad (24)$$

Note that at critical point above equations system are not converged and we used lagrangiane polynomial for extrapolation.

### Discussion and results

For show prepared computer program efficiency, methane system is selected and results are drew and compared with experimental data, which conclusions are in table 1 and figures 2 and 3. As it is seen, absolute deviation average is about 1.59 percent for saturated pressure, 0.97 percent for saturated liquid specific volume and 1.9 percent for saturated vapor specific volume.

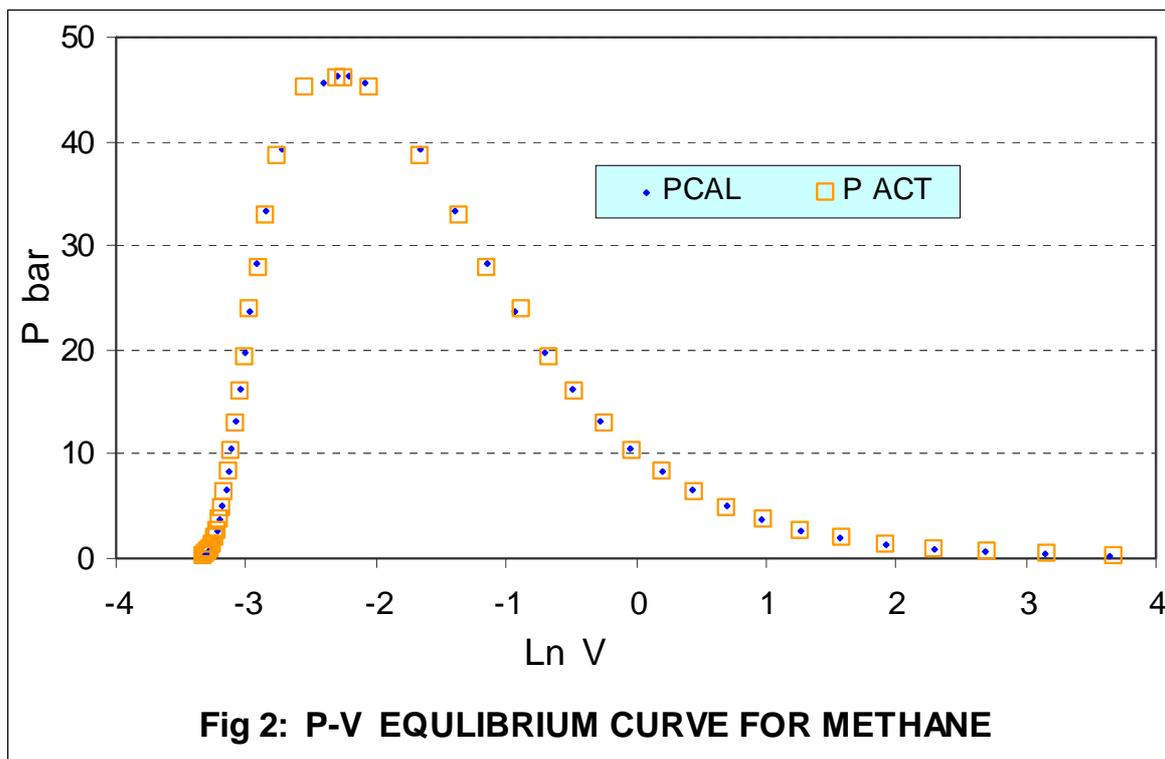
Just as shown in table and graphs, P-R equation of state will be able to cover experimental points very well. Thus it is good for design calculations in methane system.

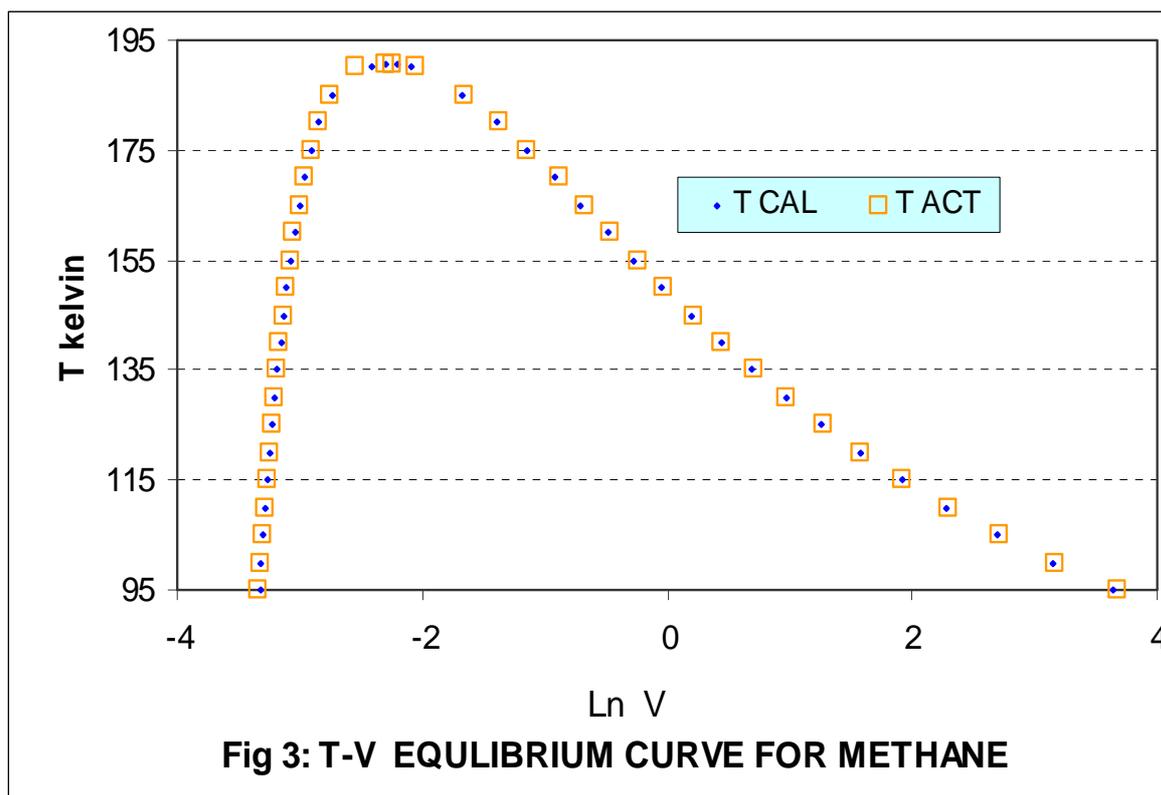


**Fig1** Computer program flowchart

**Table1** Equilibrium calculations results for methane

T (°K)	P (bar)		$V_L \cdot 10^3 (m^3/Kmol)$		$V_G (m^3/Kmol)$	
	Act.	Cal.	Act.	Cal.	Act.	Cal.
95	0.198	0.204	35.800	35.895	39.408	38.380
100	0.345	0.353	36.450	36.463	23.664	23.238
105	0.565	0.578	37.060	37.061	15.040	14.812
110	0.884	0.901	37.650	37.694	10.000	9.859
115	1.325	1.350	38.340	38.366	6.880	6.805
120	1.919	1.952	39.010	39.083	4.896	4.844
125	2.693	2.738	39.800	39.850	3.568	3.539
130	3.681	3.739	40.580	40.676	2.672	2.643
135	4.912	4.990	41.500	41.570	2.032	2.011
140	6.422	6.524	42.430	42.546	1.568	1.554
145	8.246	8.376	43.550	43.620	1.232	1.216
150	10.410	10.584	44.670	44.815	0.976	0.961
155	12.970	13.182	46.110	46.159	0.784	0.766
160	15.940	16.211	47.540	47.700	0.624	0.614
165	19.390	19.710	49.520	49.490	0.512	0.493
170	23.810	23.710	51.490	51.660	0.416	0.396
175	27.810	28.270	54.700	54.380	0.320	0.316
180	32.860	33.410	57.900	58.060	0.256	0.248
185	38.590	39.190	63.670	65.470	0.192	0.189
190	45.200	45.654	78.400	89.680	0.128	0.124
190.6	45.990	46.340	99.728	100.24	0.960	0.110
ABS.	1.59 %		0.97 %		1.88 %	





### Abbreviations

a, b, $\alpha$ , $\beta$ : Peng Robinson equation of state parameters	$\omega$ : Acentric factor
$f^L$ : Liquid phase fugacity	$G'$ : Derivation of G
$f^G$ : Gas phase fugacity	$\Delta$ : Determinant
$\Phi$ : Fugacity coefficient	f, g: Functions
P: Pressure	Subscripts and Superscripts:
T: Temperature	C: Critical properties
V: Volume	i: Calculations No.
R: Universal gas constant	L: Liquid phase properties
v: Molar volume	V: Vapor phase properties

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