Pseudocritical Constants for Gas Mixtures

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Among a number of methods for predicting the *PVT* behavior of gas mixtures, one of the simplest is the use of the compressibility-factor chart and Kay's rule for pseudocritical constants. The Beattie-Bridgman equation gives good results but is tedious. Recently methods based upon a statistico-mechanical treatment of suitable molecular models have appeared. The method of the present note is intended to give a quick estimate from limited empirical data. Although its precision and generality are less than those of the more basic approaches, it is considerably superior to Kay's rule, which is still widely used.

Using Kay's rule one assumes that the pseudocritical temperatures and pressure of gaseous mixtures are linear combinations of those of the components. However the deviations from actual data are considerable. In this work the pseudocritical values for a number of gas mixtures were determined and compared with Kay's rule. It was hoped that systematic deviations would be found and that a general treatment of the deviations would be possible.

PROCEDURE

The data of Su as reported by Seferian (6) were used in constructing the compressibility-factor chart, which was used as the generalized compressibility-factor plot. For each isotherm of the μ chart the minimum value of the compressibility factor was plotted vs. reduced pressure (Figure 1). The corresponding values of reduced temperature are noted on the curve. Note that the minimum compressibility factor for a chosen isotherm corresponds to a particular value of reduced temperature and pressure.

For example, suppose that for a certain gas mixture the isotherm minimum in compressibility factor occurs at 585°R. and 127 atm. and that the compressibility factor at that point is 0.80. From Figure 1 the reduced temperature and pressure for that point are 1.50 and 3.44, respectively. The pseudocritical temperature, which will be called the *experimental pseudocritical*, is then 585/1.50 = 390°R., and the experimental pseudocritical pressure is 127/3.44 = 36.9 atm.

In some cases adjusted pseudocriticals are also reported. These give a better fit to the entire isotherm than those values determined by the simple procedure.

Table 1. Pseudocriticals for Carbon Dioxide

Temperature, °F.	Pseudocriticals: Temperature, °R.	Pseudocriticals: Pressure, atm.
100	550	85.0
160	547	75.5
220	545	63.3
280	536	75.1
340	531	72.7
400	521	71.3
460	504	69.4
Average	535	73.2
True critical	547.7	73.0

RESULTS

As a first example of the use of the method, pseudocritical values for carbon dioxide were calculated from the data of Reamer, Olds, Sage, and Lacey (2). The values for isotherms from 100° to 460°F., obtained by the use of the minima chart, are given in Table 1.

The pseudocritical values for methane-propane mixtures are given in Table 2. Both the approximate values calculated from the minima chart and adjusted values for good fit along the

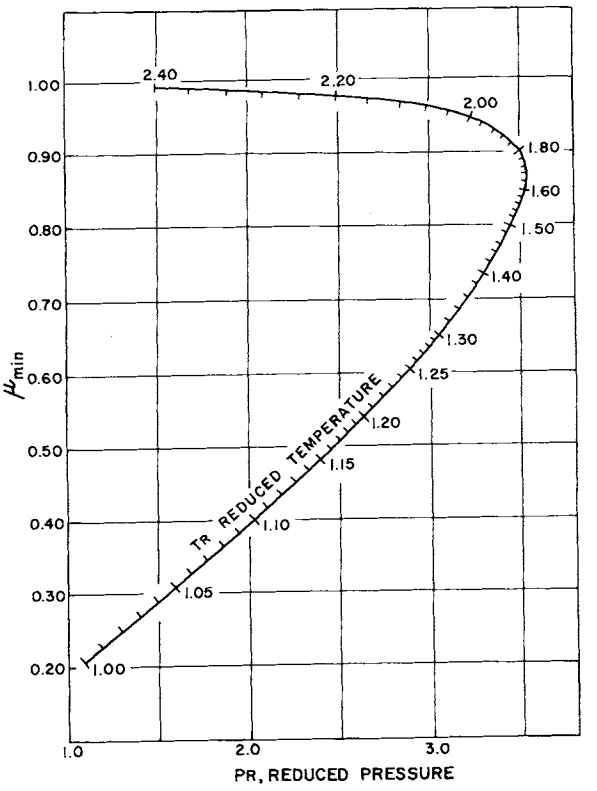

Fig. 1. Plot of μ-chart minima.

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isotherm are given in some cases. If only one value is given, it is the approximate value.

In Table 3 a typical comparison for calculated and observed compressibilities is given. The comparison is made for a mixture of 60% methane and 40% propane at 55°C. In Figure 2 are shown the deviations of the experimental pseudocritical values from those predicted by Kay's rule for this mixture.

DISCUSSION

It is seen that the method used here allows a facile determination of approximate pseudocriticals for a gas or a gas mixture, provided that an isotherm has been determined in the region of $1 \leqq T_r \leqq 2$. Once the approximate values are known, it is a relatively simple matter to adjust the values empirically to provide a good fit to the entire isotherm. The method gives a very good value for the pseudocritical temperature, and little adjustment is needed. However because of the low curvature of the isotherm near the minimum, it is frequently found that the pseudocritical pressure requires substantial adjustment.

The deviations of the pseudocriticals from Kay's rule are seen to be substantial. The deviations are positive for both pressure and temperature for the system methane-propane but are symmetrical for temperature only. The deviations for methane-ethane (*5*) and methane–*n*-butane (*4*) are similar but not identical. The deviations of the hydrocarbons and carbon dioxide, including those for methane–carbon dioxide (*2*), ethane–carbon dioxide (*3*), and *n*-butane–carbon dioxide (*1*), are substantially negative. Thus it seems unlikely that an over-all generalization can be made regarding the deviations. However because of the similarity of the deviations in similar systems limited generalizations are possible, and these generalizations give considerably better estimates of the compressibility factor than does Kay's rule.

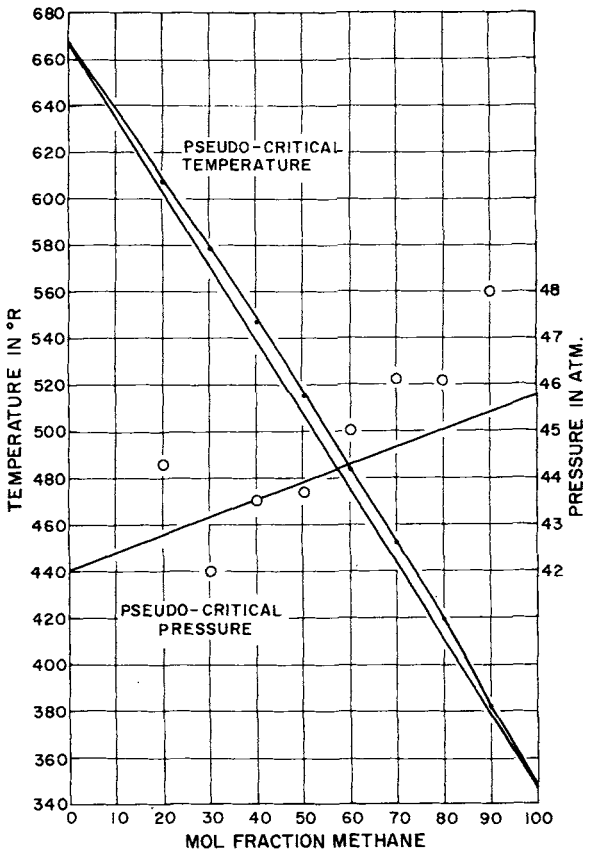

Fig. 2. Pseudocriticals, methane-propane.

Table 2. Pseudocriticals, Methane-Propane
(First value is approximate, second is adjusted)
Mole fraction methane

Temperature, °C.	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
				Pseudocritical temperature, °R.				
20							417, 417	381, 377
40					484, 484	452, 452	418, 417	384
55				514	482, 484	448, 451	415, 417	378
70			549	515	485	453, 451	418, 418	382
90	607	579	547	517	482	454, 454	415, 424	389
				Pseudocritical pressure, atm.				
20							46.6, 46.6	50.5, 47.0
40					43.3, 44.5	46.8, 45.5	43.9, 45.5	48.8
55				42.8	38.2, 44.5	48.0, 45.5	45.5, 46.6	48.7
70			43.7	45.0	47.0	51.4, 48.0	49.8, 48.0	48.7
90	44.3	42.0	43.3	43.2	44.0	46.4, 45.5	42.2, 44.0	45.9

Table 3. Compressibility Factor, Methane-Propane
0.60 mole fraction methane, 55°C.

Pressure, atm.	Experimental compressibility	Calculated compressibility Adjusted-fit values $T_c = 484$°R., $P_c = 44.5$ atm.	Calculated compressibility Kay's rule $T_c = 472.8$°R., $P_c = 44.3$ atm.
20	0.920	0.913	0.920
40	0.847	0.825	0.841
60	0.739	0.737	0.754
80	0.655	0.650	0.687
100	0.602	0.590	0.635
120	0.575	0.569	0.609
140	0.583	0.579	0.610
160	0.604	0.604	0.627
180	0.631	0.637	0.655
200	0.664	0.665	0.687

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