tions. In each instance the static value at 35° fell a little above a straight line drawn between 30° and 40°. This is consistent with a decrease in the latent heat with increasing temperature. Some of Copp's 35° points fell above the line and some below. This does not prove Copp's values wrong, only that the static values are self consistent while not consistent with Copp's values. Both of the 35°C. total pressure curves were numerically integrated to obtain vapor compositions. The maximum difference in vapor composition occurs at 75 mole % amine in the liquid. At this point Copp's data yield an amine fraction of 0.865 in the vapor while the static data give 0.874.

ACKNOWLEDGMENT

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Liquid-Vapor Equilibrium in the System Helium-Methane

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Liquid and gas phase compositions for the system helium-methane have been measured at 15° intervals from 95° to 185°K. up to 200 atm. pressure. Data for these seven isotherms were taken in a gas phase recirculation apparatus with chromatographic analysis. In most regions the phase compositions obtained are thought to be within ± 3% of the mole fraction of the minor component. The maximum deviation from the enhancement factor curve at the lowest concentration levels was 16%. These data are in excellent agreement with most of the very recent data but are in poor agreement with the older data for this system.

Until recently, data for the helium-methane system were very limited in the liquid-vapor region and nonexistent in the solid-vapor region. Prior to the present investigation measurements were made to determine the gas phase compositions in equilibrium with the solid phase in the helium-methane system from the triple-point temperature to as low a temperature as possible consistent with quantitative analysis limitations of the sensitive hydrogen flame-ionization technique (*1*). In that investigation, gas phase compositions were measured in the liquid-vapor region along the 91.00°K. isotherm for direct comparison with the existing data. Those measurements indicated that the data of Kharakhorin (*2*) at 91.1° were incorrect and suggested that data from the latter source in the higher temperature region might also be questionable.

The purpose of the present investigation was to measure the phase equilibria properties of the helium-methane system over the entire liquid-vapor region from a temperature just above the methane triple point to a temperature near the methane critical point. Compositions of both phases were determined chromatographically, with thermal conductivity detection, at 15° intervals from 95° up to 185°K. at total pressures up to 200 atm. The region studied in the present investigation essentially completes the coverage of this system within practical limits and provides a good comparison with all other equilibria data available for this system.

EXPERIMENTAL METHODS

The experimental apparatus used in this investigation, described in detail elsewhere (*3*) is a closed-loop flow system in which the gas phase is recirculated through the equilibrium cell by a magnetically operated pump at ambient temperature. The recirculated gas phase also passes through a ballast volume (in an ambient temperature water bath) which allows the removal of small samples of either phase from the system with no detectable change in system pressure. The equilibrium cell within the cryostat was refrigerated with cold gas from boiling liquid nitrogen in the bottom of the cryostat. This cold gas supplied an excess of refrigeration which was counteracted by an automatically controlled heater wrapped around the cell.

System pressure was measured with two Bourdon types of gauges with ranges of 0 to 100 and 0 to 300 atm. These gauges had a maximum error rating of ± 0.1% full scale. The temperature at the top of the cell was measured by a platinum resistance thermometer calibrated on the 1955 NBS temperature scale. The small difference between the top of the cell and the lower interior, where equilibrium was established, was measured with a gold-2.1 at. % cobalt vs. copper differential thermocouple. In all cases this temperature difference was no more than 0.20°K. with the top of the cell warmer than the bottom. The temperatures reported are the platinum resistance thermometer indication adjusted by the average differential observed for all points of the isotherm. Maximum deviation from this average was ± 0.05°K.

Samples of the equilibrium phases were analyzed for the minor component by thermal conductivity detection with a gas chromatograph in conjunction with a digital integrating voltmeter for peak area measurements. Argon was used as the carrier gas. The analyzer was calibrated with prepared mixtures at 10.4 and 50.9% methane in helium and 10.1% helium in methane. Calibration points were obtained at intermediate values by utilizing the prepared standards at different sample pressures. In addition the analyzer was calibrated after each sample at approximately the same concentration level of the component being analyzed. Analyses were quite consistent, and the maximum error is thought to be ± 3% of the mole fraction of the minor component, except at the lowest concentration levels.

The helium used in this investigation was U.S. Bureau of Mines grade A helium with about 15 p.p.m. of neon the major impurity. Two different commercial grades of methane were used, a research grade of 99.8% minimum purity and an ultrapure grade with 99.95% minimum purity, with no noticeable difference in results.

RESULTS AND DISCUSSION

Equilibrium phase compositions in the liquid-vapor region of the helium-methane system were determined at nominal temperatures of 95.00°, 110.00°, 125.00°, 140.00°, 155.00°, 170.00°, and 185.00°K., as indicated by the platinum resistance thermometer, up to 200 atm. pressure. The actual equilibrium temperatures, as discussed above, are given in Table 1 along with the experimental values of mole percent methane in the gas phase and mole percent helium in the liquid phase. Values of methane vapor pressure used in this work were calculated from the expressions given by Kirk (*4*) based on the 1955 NBS temperature scale.

From these data the helium and methane *K* factors (ratios of mole fraction in the gas phase to that in the liquid) shown in Figures 1 and 2 were calculated. Since compositions of both phases approach values of nearly pure components, particularly at the lower temperatures and moderate pressures, the methane *K* factors primarily reflect variations in the concentration of methane in the gas phase, while helium *K* factors primarily reflect variations in the concentration of helium in the liquid phase. These curves exhibit the usual trend for systems in which the solubility of the gas in the liquid increases with increasing temperature.

In Figure 3 a comparison is made, at ($\pi - p_{01}$) equal

TABLE 1. EXPERIMENTAL LIQUID-VAPOR EQUILIBRIUM DATA FOR THE SYSTEM HELIUM-METHANE

T, °K.	p_{01}, atm.	π, atm.	100 x_2, mole % He in liquid	100 y_1 mole % CH_4 in gas
94.97	0.1954	4.75	0.012	4.20
±0.02		10.05	0.034	1.90
		20.00	0.069	1.00
		39.75	0.136	0.595
		60.00	—	0.434
		69.00	0.226	—
		84.60	0.274	0.363
		90.30	0.285	—
		117.4	0.363	0.253
		142.6	0.419	0.231
		161.9	0.472	0.196
		180.4	—	0.210
		192.0	0.524	—
124.85	2.639	11.20	0.125	25.9
±0.03		20.20	0.216	14.3
		40.20	0.499	7.90
		63.60	0.799	5.17
		85.50	1.04	3.95
		112.2	1.31	3.07
		142.5	1.60	2.58
		171.7	1.84	2.22
		201.3	2.09	2.01
139.83	6.286	22.80	0.447	29.8
±0.03		39.20	0.789	18.8
		62.40	—	12.4
		81.80	1.63	9.45
		112.0	2.14	7.42
		142.4	2.62	—
		172.0	3.04	5.23
		199.0	3.41	4.73
169.81	22.864	32.50	0.640	78.3
±0.05		55.30	2.06	53.1
		58.00	2.17	—
		66.90	2.61	—
		82.00	3.52	39.9
		107.2	4.69	33.1
		114.6	4.99	—
		141.9	6.12	26.2
		168.6	7.16	23.0
		195.9	8.06	—
109.90	0.8630	20.15	0.151	4.63
±0.02		35.20	0.262	2.79
		41.00	0.304	2.44
		70.30	0.488	1.49
		89.80	0.604	1.22
		101.5	—	1.08
		102.0	0.679	—
		131.4	0.833	0.948
		162.6	0.978	0.822
		190.5	1.11	—
		199.1	—	0.721
154.80	12.685	17.40	—	78.8
±0.04		37.20	1.03	—
		43.10	1.30	36.8
		62.30	1.89	—
		78.60	—	21.5
		79.50	2.35	—
		108.5	3.19	—
		108.9	—	16.2
		143.0	4.13	12.9
		171.6	4.80	10.8
		201.2	5.37	10.0
184.83	37.887	44.50	—	93.07
±0.05		66.60	3.52	78.8
		87.50	—	66.9
		88.00	5.58	—
		111.9	7.73	56.4
		152.4	11.1	48.1
		178.0	12.6	43.8
		202.6	13.7	40.8

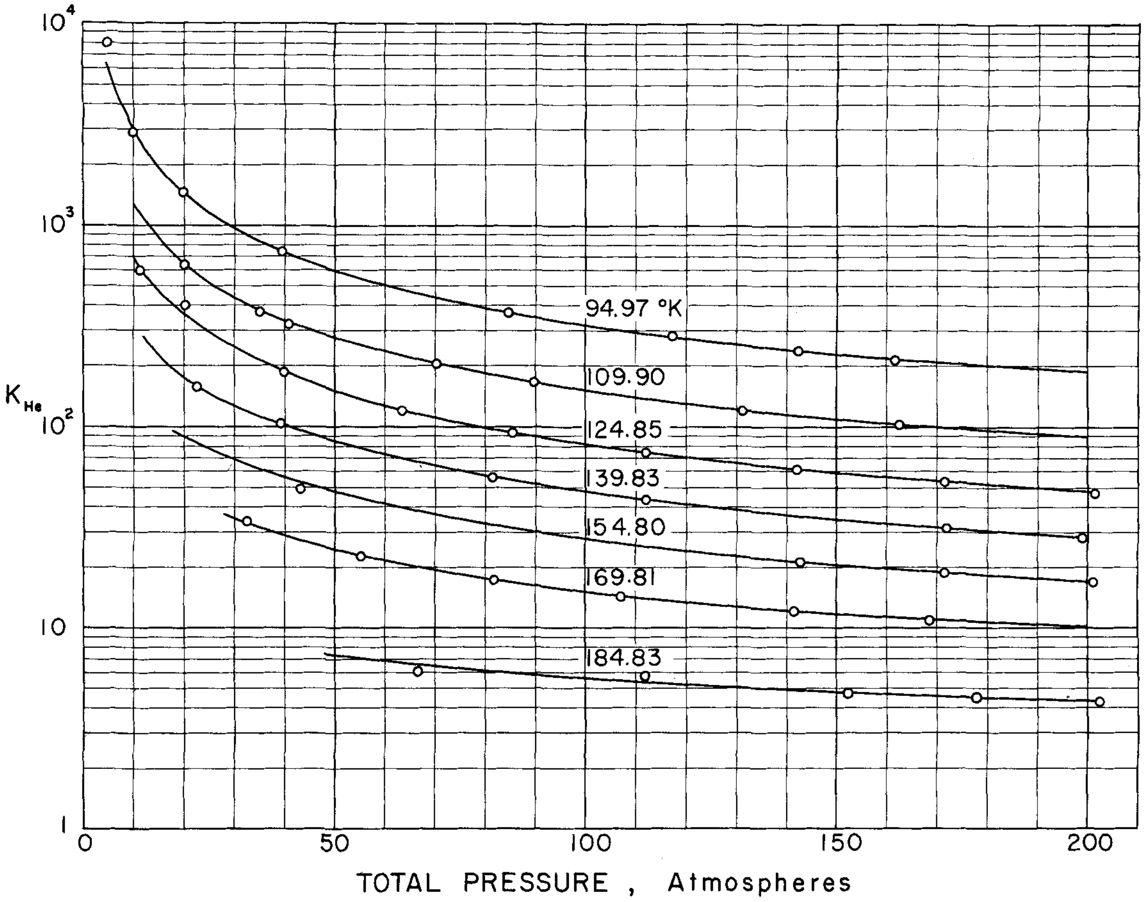

Fig. 1. Helium K factors.

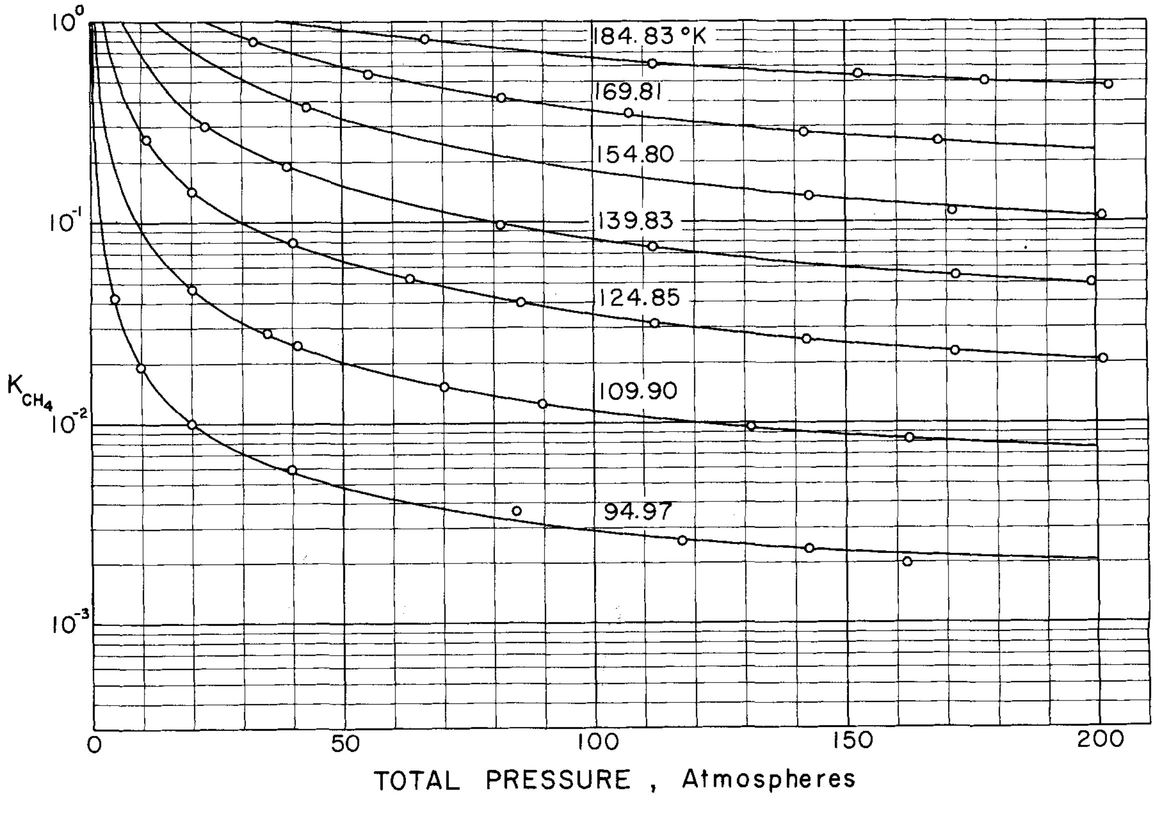

Fig. 2. Methane K factors.

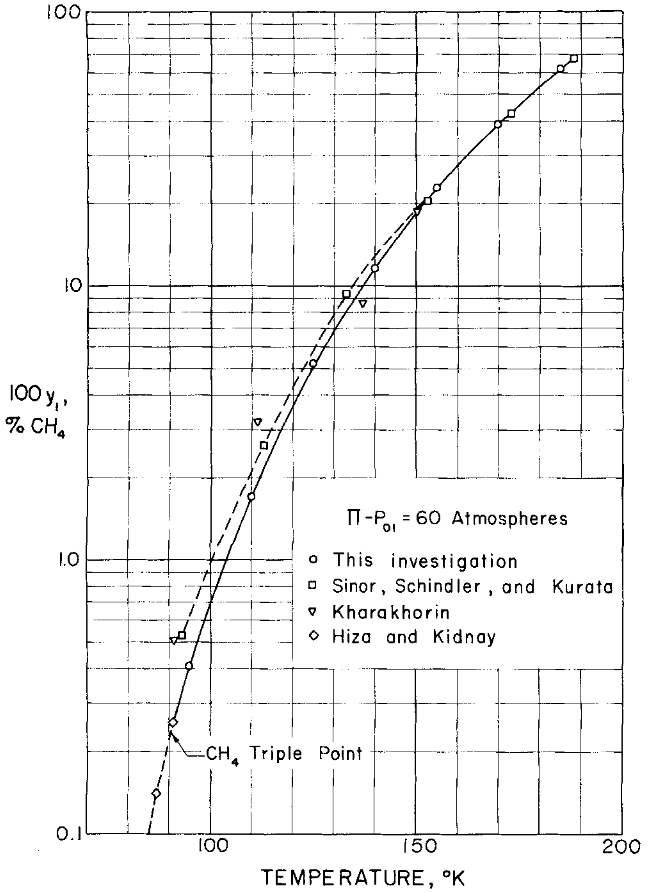

Fig. 3. Cross plot methane concentration in the gas phase at $\pi - p_{01}$ = 60 atm., comparison with other data.

to 60 atm., of the gas phase compositions with those of Hiza and Kidnay, Kharakhorin, and the very recent values of Sinor et al. (5). Data used from the first source include an isotherm each above and below the methane triple point. The present data are in excellent agreement with the data of Hiza and Kidnay and with the data of Sinor et al. above 140°K. The data from the latter source are consistently high below 140°K. The data of Kharakhorin are inconsistent and appear to agree better with the present data above 130°K. and with the data of Sinor et al. below 130°K. Similar deviations are found at lower pressures, but at 130 atm. helium pressure the data of Sinor et al. at 93.15° are in good agreement with the present data.

A sensitive method of evaluating such discrepancies in gas phase data is comparison of enhancement factors, that is, the ratios of methane partial pressure to the normal vapor pressure. Isothermal values of the enhancement factor when plotted on a semilog plot must originate at unity at the normal vapor pressure and generally increase in some uniform manner with an increase in total pressure. Also, for a nearly ideal system such as the helium-methane system, isobaric values of the enhancement factor in the middle and lower temperatures of the liquid-vapor region do not change rapidly with temperature.

Enhancement factors for the isotherms between 90° and 95°K. are compared in Figure 4. From the work of Hiza and Kidnay it would be expected that enhancement factors for all of these isotherms should fall on the same curve for all practical purposes. The present data do fall on the same curve as the data of Hiza and Kidnay but scatter more because of less sensitive analyses at this concentration level. The enhancement factors of Sinor et al. do not approach unity at the lowest pressure and are as much as 80% higher. The data of Kharakhorin are considerably higher and much more inconsistent. Both

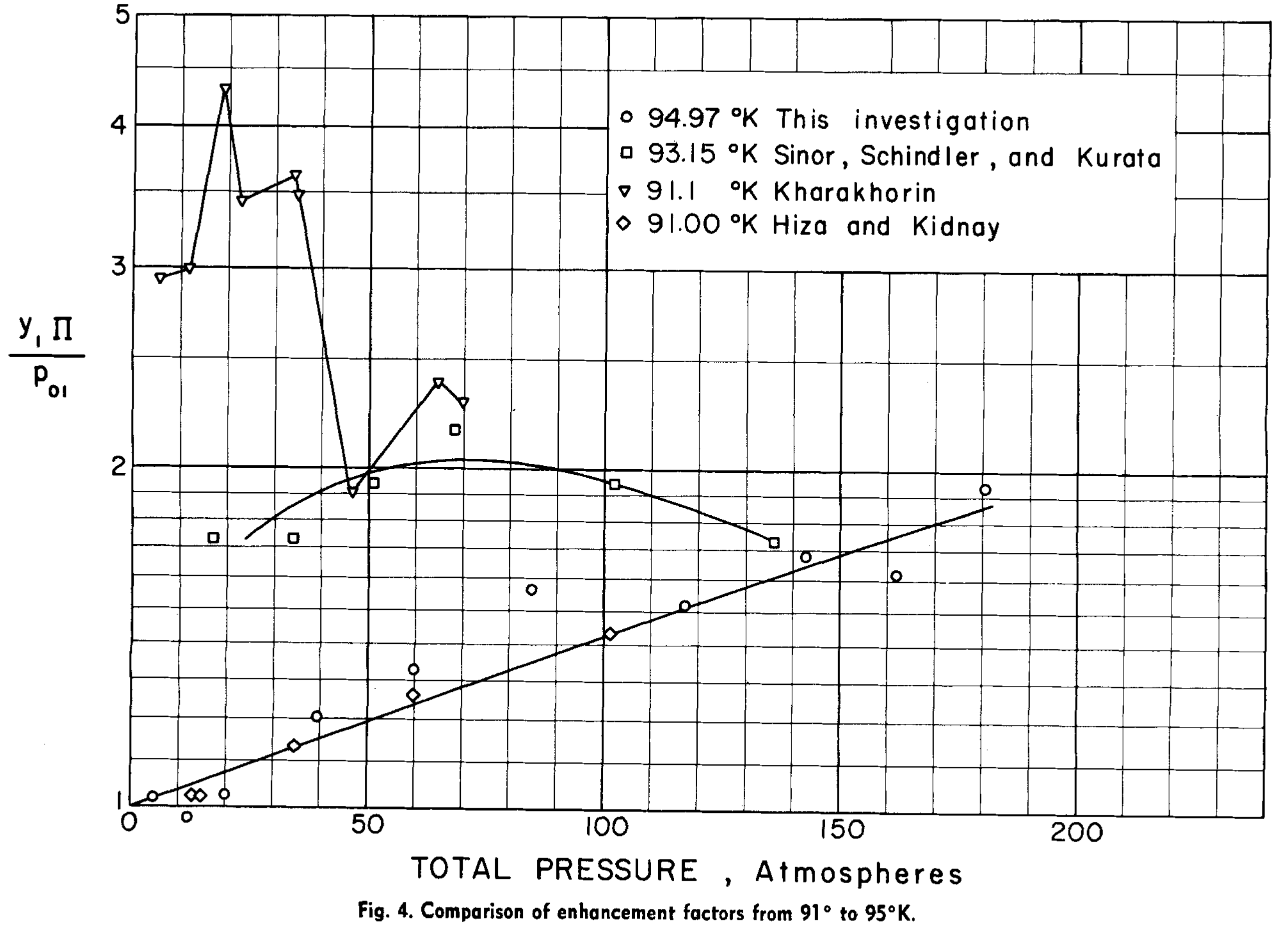

Fig. 4. Comparison of enhancement factors from 91° to 95°K.

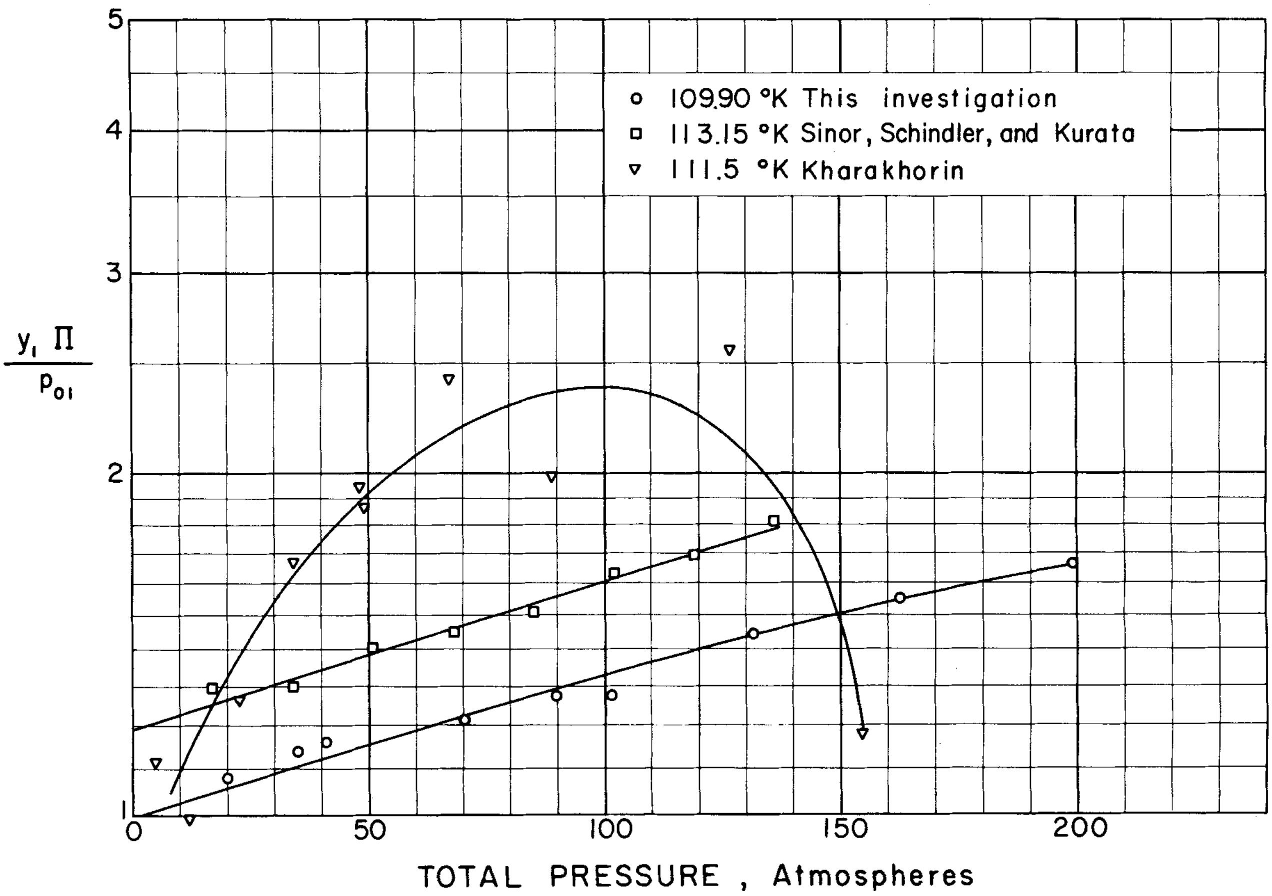

Fig. 5. Comparison of enhancement factors from 110° to 113°K.

the latter isotherms also show an apparent maximum in the enhancement factors which has no theoretical basis, at least at these temperatures and pressures.

In Figure 5 enhancement factors at 109.90°K. are compared with those of Sinor et al. at 113.15° and Kharakhorin at 111.5°K. Kharakhorin's values appear to start correctly at the lowest pressure but increase rapidly to an apparent maximum and at the highest pressure scatter badly. The values of Sinor et al. are very consistent but are uniformly higher than values from the present investigation by approximately 20%; the curve through the data of Sinor et al. intercepts the zero pressure axis at 1.19. At temperatures above 140°K. the gas phase data of Sinor et al. and of this investigation are in agreement within experimental error.

In Figure 6 a comparison is made, at ($\pi - p_{01}$) of 60 atm., of the liquid phase compositions with those of Sinor et al., Kharakhorin, and Gonikberg and Fastovskii (6). While the data of Kharakhorin are much higher at all temperatures, the data of Gonikberg and Fastovskii are not quite as high at 90.3°K. and are in fair agreement with the present data at 106.0°K. The data of Sinor et al. are in excellent agreement with the present data, particularly in the low temperature end. These data are higher than the present data by 6% at 133.15°K., 10% at 153.15°K., and 6% at 173.15°K. Similar deviations were noted at higher pressures, but the data are in better agreement at lower pressures.

In the liquid phase a sensitive method of detecting isothermal inconsistencies is a Henry's law type of plot of the data. In Figure 7 a semilog plot of $\pi - p_{01}/x_2$ vs. $\pi - p_{01}$ is shown to compare the present data with those of Sinor et al. Both sets of data appear to be self-consistent on individual isotherms, but the isotherms of Sinor et al. at the intermediate temperatures exhibit a noticeable dif-

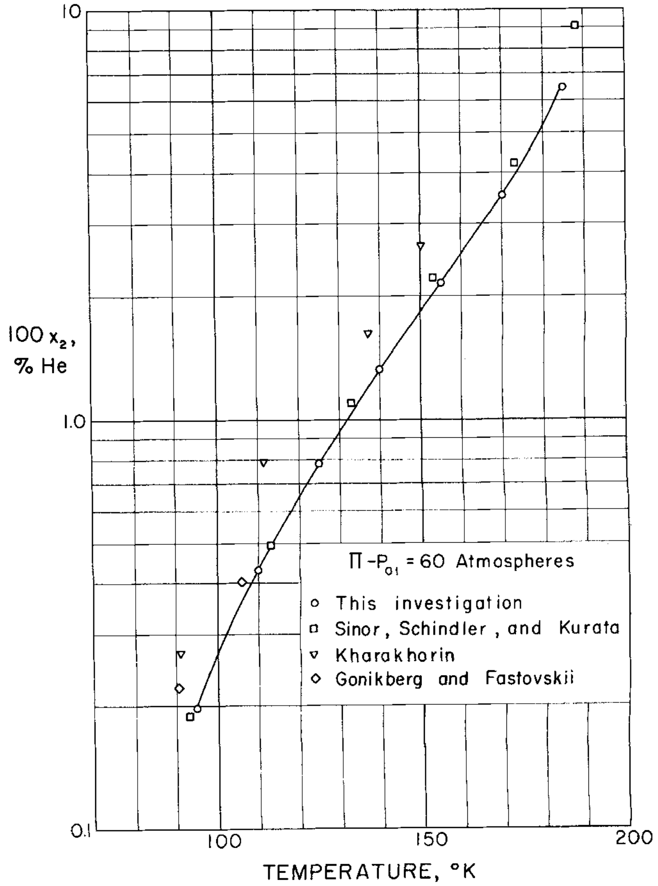

Fig. 6. Cross plot of helium concentration in the liquid phase at $\pi - p_{01} = 60$ atm., comparison with other data.

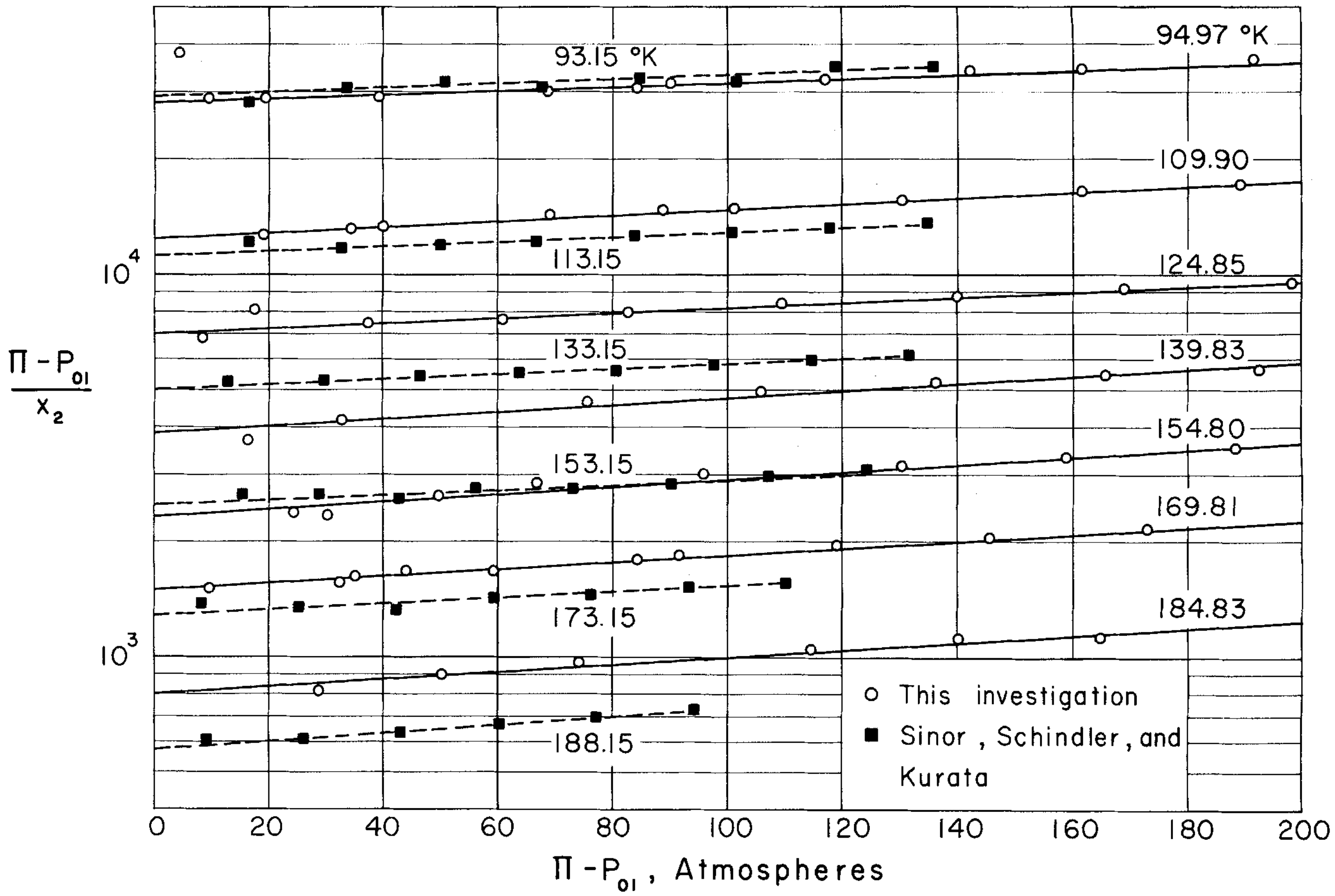

Fig. 7. Henry's law correlation of the liquid data, comparison with data of Sinor et al.

ference in slope when compared with the present data. This difference, on comparison with Figure 6, is seen to result from discrepancies not much greater than the combined experimental errors.

To test the spacing of the isotherms at different pressures pseudo heats of solution have been calculated from helium K factors at 40, 50, 60, 80, and 100 atm. total pressure from the following equation:

$$\Delta H_s = -2.303R\left(\frac{T'T}{T'-T}\right)\log\frac{K_2}{K'_2} \qquad (1)$$

postulating ideal behavior in both phases (7). As stated earlier, although the helium K factors include gas phase compositions, they primarily reflect discrepancies in the liquid phase composition. The discrepancy between the gas phase compositions of Sinor et al. and of the present investigation at the low temperatures has no effect on the helium K factors since the gas phase is so nearly pure helium. Values of ΔH_s obtained from both sets of data are compared in Figure 8. The general trend is for ΔH_s to decrease with increasing pressure. From the present data, values of ΔH_s from the 109.90° and 124.85° isotherms and the 124.85° and 139.83° isotherms exhibit opposite trends and are inconsistent with the other data below 60 atm. pressure. It is logical to conclude that the spacing of the common isotherm, 124.85°, is incorrect below 60 atm. By the same argument values of ΔH_s from data of Sinor et al. from the 133.15° and 153.15° isotherms and the 153.15° and 173.15° isotherms indicate that the spacing of their 153.15° isotherm is incorrect more generally over the pressure range considered. Other than these apparent discrepancies, there is no general difference in the magnitude and in the dependence of ΔH_s values on temperature and pressure. Thus it is not possible to conclude that one set of liquid phase data is more correct than the other.

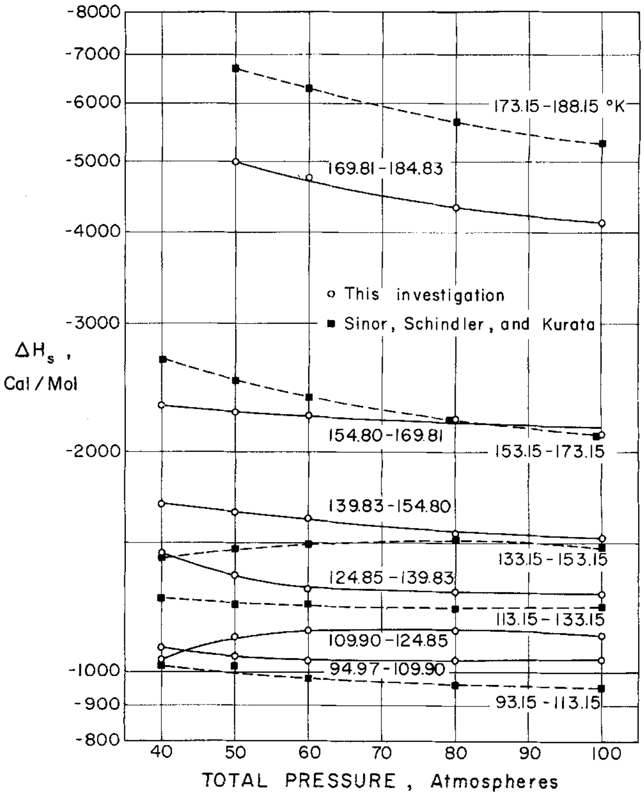

Fig. 8. Pseudo heats of solution from helium *K* factors, comparison with data of Sinor et al.

SUMMARY

The liquid-vapor data up to 200 atm. given here along with the liquid-vapor data up to 136 atm. of Sinor et al. and the solid-vapor data up to 140 atm. of Hiza and Kidnay provide a fairly complete set of consistent phase equilibria data for the helium-methane system. The major discrepancy between the sets of data occurred in the gas phase and in a temperature region where a simple test with enhancement factors shows that the present data follow a more reasonable course than those of Sinor et al. The isobaric consistency test applied indicates the probability that one isotherm in each set of liquid phase data is suspect in at least a portion of the pressure range, but in general the discrepancies are not very large. These new data provide adequate evidence that the old data of Kharakhorin and, to a lesser extent, those of Gonikberg and Fastovskii, are incorrect. Measurements of the three-phase locus and possibly some confirming measurements in the regions just below and above the triple-point temperature of methane and near the critical temperature of methane would be a valuable addition to the data for the helium-methane system.

NOTATION

ΔH_s = pseudo heat of solution, as defined by Equation (1)
K = ratio of mole fraction in gas phase to that in the liquid phase
p_0 = vapor pressure, atm.
T = temperature, °K.
x = mole fraction in liquid phase
y = mole fraction in gas phase
π = total pressure, atm.

Subscripts

1 = methane
2 = helium
0 = pure component

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Three Turbulent Drag Coefficients in Beds of Spheres

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Form, shear, and total drag have been studied in the 2,500 to 65,000 range of Reynolds number over a wide range of porosity by using the data of Thodos and co-workers. The effect of Reynolds number was found to be the —0.14 power for form drag, the —0.19 power for total drag, and the —0.5 and higher power for shear drag, so that the ratio of shear drag to total drag decreased from about 16% to less than 5% with increasing Reynolds numbers. For the 2,500 to 6,000 range of Reynolds number, experimental evidence supports the apparently analogous behavior between average shear drag and average heat flux. Limitations and related evidence of this behavior are also discussed. Methods are suggested for estimating drag ratios and coefficients by using the correlation of this work.

Where the same characteristic area and velocity are used to define drag coefficients, the total drag may be considered as equal to the sum of the shear drag and the pressure (or form) drag as follows:

$$f_t = f_s + f_p \qquad (1)$$

Knowledge of the interrelationships of these types of drag over a range of velocities contributes to the understanding of several phenomena, including the relative contributions of shear and form drag, the relationship between transport rates and pressure drop, and the differences among the mechanisms. Such understanding would be helpful in the determination of optimum flow rates.

Consider the case of turbulent flow in particulate beds. Although the total drag is relatively easy to determine from pressure drop measurements, shear drag and form drag are more difficult to measure. No direct measurements of shear drag have been reported and only recently have any precise measurements of form drag in beds of solids become available (*16*). The form drag work of Wentz and Thodos (*16*) has special importance because total drag was also measured on the same beds at the same conditions.

It might seem that the dependence of shear drag on velocity could easily be determined from Equation (1) and the existing correlations for form drag and total drag