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Compressibility, Second and Third Virial Coefficients, and Interaction Second Virial Coefficients of Mixtures of Propane–Helium and Propene–Helium

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Compressibility factors, the second and the third virial coefficients of mixtures, and the interaction second virial coefficients of propane + helium and propene + helium systems have been determined by the Burnett method at 393.2, 407.5, 423.0 K in the pressure range from 425 to 6870 kPa.

1. Introduction

The compressibility factor Z of real gases describes deviations from ideal gas properties. It is convenient to express the compressibility factor by the virial equation of state

$$Z = P/\zeta RT = 1 + B(T)\zeta + C(T)\zeta^2 + \ldots \tag{1}$$

where P is gas pressure, ζ is density, R is gas constant, T is absolute temperature, and $B(T)$, $C(T)$, ..., are virial coefficients. Virial coefficients have a firm basis in theory and are derived from the knowledge of the potential energy of molecular interaction by means of statistical thermodynamics of the gas phase.

In this work, the Burnett method (1) has been employed for the investigation of mixtures. In contrast with other PVT methods, that of Burnett does not require the knowledge of mass or volume.

Up to now a correlation for hydrocarbon + helium mixtures does not exist, and our knowledge about their molecular interactions is very meager (6).

2. Experimental Section

Purity of Substances. The purity of helium used for the experiments was 99.995 vol %. Propane and propene were stored in the commercial pressure cylinder of Fluka A.G. Chemische Fabrik. The purity of 99.9% given by the manufacturer was confirmed by the GLC method.

Description of the Method of Measurements. The scheme of the apparatus is shown in Figure 1. A more detailed description of the method and apparatus can be found elsewhere (7–9) along with the details of the calibration of the dead weight gauge. The temperature was measured with a Tinsley Pt

thermometer (5187SA) calibrated at the National Physical Laboratory, Teddington Middlesex, England.

The experiment is based on temperature and pressure measurements in a series of isothermal gas expansions from V_I (volume limited by valves 1 and 4 and the membrane of the differential pressure indicator III) to the volume $V_I + V_{II}$ (volume V_{II} being included between valves 1 and 2). Each expansion follows evacuation of the gases from the volume V_{II}. The series of measured pressures P_1, P_2, ⋯, P_r in the isothermal experiment is called an expansion run. The following equations can be derived for the Burnett method

$$\frac{\zeta_{r-1}}{\zeta_r} = AN_r = AN_\infty \xi_r = AN_\infty \left[\frac{1 + a10^{-6}P_r}{1 + b10^{-6}P_{r-1}} \right] \tag{2}$$

$$\zeta_1 = \zeta_r AN_\infty{}^{r-1} \prod_{i=1}^{r-1} \xi_i \tag{3}$$

where AN_∞ is the apparatus constant and ξ_r is the correction for the isothermal pressure deformation of the apparatus. The constants a and b are given elsewhere (7, 8).

The method makes possible the preparation of mixtures by condensation of one component directly in the apparatus. A sample of propane or propene of known mass, sealed in a glass ampole, was placed in crushing chamber IV. After evacuation of the volumes $V_I + V_{III}$ (volume V_{III} is a part of a chamber limited by valve 4), valve 1 was shut and reservoir I was frozen with liquid nitrogen in a Dewar flask. Then, the ampole was crushed by means of a special valve in the heated chamber IV.

After complete condensation of the hydrocarbon, valve 4 was shut and the Burnett apparatus was heated to working temperatures between 393 and 423 K. The pressure P_{01} of propane or propene in volume V_I was measured after thermal equilibrium had been achieved. Then expansion reservoir I was cooled again with liquid nitrogen. In the meantime, the volume contained between valves 1 and 3 after its previous evacuation to pressures of the order of 5×10^{-4} Torr was filled with helium. The quantity of helium was roughly estimated from the valve of volume V_{II} and the pressure measured with a Bourdon-type manometer, V. Helium was then forced into reservoir I by a rapid opening of valve 1. Pressure was measured again when

Table I. Compressibility Factors, Virial Coefficients, and Apparatus Constants for the Propane-Helium System (atm = 101.325 kPa)

Run No. 1: $T = 393.18$ K, $x_I = 0.7672$, $B_I(T,x) = -111.85$ cm^3 mol^{-1}, $C_I(T,x) = 9934.9$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.57282$, $x_{II} = 0.7696$, $B_{II}(T,x) = -111.18$ cm^3 mol^{-1}, $C_{II}(T,x) = 9684.7$ (cm^3)^2 mol^{-2}, $AN_{\infty II} = 1.57264$

r	P_r/atm	Z_{rI}	Z_{rII}	r	P_r/atm	Z_{rI}	Z_{rII}
1	61.8338	0.786 40		5	12.3000	0.957 01	0.957 25
2	42.5241	0.850 51	0.851 03	6	7.9461	0.972 30	0.972 46
3	28.5947	0.899 42	0.899 89	7	5.1039	0.982 24	0.982 35
4	18.8765	0.933 81	0.934 16				

Run No. 2: $T = 393.19$ K, $x_I = 0.7063$, $x_{II} = 0.7084$, $B_I(T,x) = -87.88$ cm^3 mol^{-1}, $C_I(T,x) = 7999.3$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.56499$

r	P_r/atm	Z_{rI}	r	P_r/atm	Z_{rI}
1	63.3241	0.838 07	4	18.7208	0.949 28
2	42.8022	0.886 40	5	12.1822	0.966 90
3	28.4884	0.923 27			

Run No. 3: $T = 407.49$ K, $x_I = 0.6255$, $B_I(T,x) = -56.10$ cm^3 mol^{-1}, $C_I(T,x) = 5700.2$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.56630$, $x_{II} = 0.6273$, $B_{II}(T,x) = -58.74$ cm^3 mol^{-1}, $C_{II}(T,x) = 6750.8$ (cm^3)^2 mol^{-2}, $AN_{\infty II} = 1.56684$

r	P_r/atm	Z_{rI}	Z_{rII}	r	P_r/atm	Z_{rI}	Z_{rII}
1	61.4811	0.909 92		5	11.0260	0.981 80	0.981 02
2	40.4311	0.937 11	0.935 34	6	7.0855	0.988 23	0.987 71
3	26.3799	0.957 65	0.956 12	7	4.5422	0.992 43	0.992 08
4	17.0984	0.972 07	0.970 93				

Run No. 4: $T = 407.40$ K, $x_I = 0.4224$, $B_I(T,x) = -12.09$ cm^3 mol^{-1}, $C_I(T,x) = 2878.2$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.57263$, $x_{II} = 0.4232$, $B_{II}(T,x) = -10.23$ cm^3 mol^{-1}, $C_{II}(T,x) = 2157.2$ (cm^3)^2 mol^{-2}, $AN_{\infty II} = 1.57228$

r	P_r/atm	Z_{rI}	Z_{rII}	r	P_r/atm	Z_{rI}	Z_{rII}
1	64.1112	0.987 38		5	10.5810	0.996 45	0.996 97
2	40.8584	0.989 46	0.990 66	6	6.7368	0.997 68	0.998 02
3	26.0582	0.992 28	0.993 30	7	4.2880	0.998 49	0.998 72
4	16.6102	0.994 68	0.995 43				

Run No. 5: $T = 423.00$ K, $x_I = 0.3914$, $B_I(T,x) = -4.07$ cm^3 mol^{-1}, $C_I(T,x) = 2134.5$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.57155$, $x_{II} = 0.3918$, $B_{II}(T,x) = -2.40$ cm^{-3} mol^{-1}, $C_{II}(T,x) = 1487.9$ (cm^3)^2 mol^{-2}, $AN_{\infty II} = 1.57124$

r	P_r/atm	Z_{rI}	Z_{rII}	r	P_r/atm	Z_{rI}	Z_{rII}
1	66.9643	1.000 10		5	10.9658	0.998 93	0.999 39
2	42.5371	0.998 22	0.999 30	6	6.9822	0.999 27	0.999 58
3	27.0667	0.998 13	0.999 04	7	4.4463	0.999 51	0.999 72
4	17.2336	0.998 50	0.999 18				

Run No. 6: $T = 423.00$ K, $x_{II} = 0.8080$, $B_I(T,x) = -104.88$ cm^3 mol^{-1}, $C_I(T,x) = 9777.8$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.57104$, $B_{II}(T,x) = -104.71$ cm^3 mol^{-1}, $C_{II}(T,x) = 9714.2$ (cm^3)^2 mol^{-2}, $AN_{\infty II} = 1.57093$

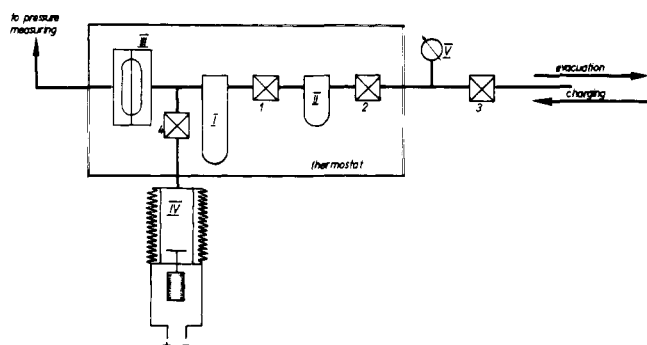| r	P_r/atm	Z_{rI}	Z_{rII}	r	P_r/atm	Z_{rI}	Z_{rII}
1	62.1976	0.816 99		5	12.0413	0.963 49	0.963 55
2	42.2904	0.872 61	0.872 75	6	7.7712	0.976 47	0.976 50
3	28.2143	0.914 50	0.914 61	7	4.9899	0.984 90	0.984 92
4	18.5363	0.943 79	0.943 87				

Figure 1. Schematic diagram of the Burnett apparatus: 1, expansion valve; 2-4, charging-venting valves; I, II, pressure chambers; III, differential pressure indicator; IV, crushing chamber; V, Bourdon-type manometer.

the temperature became stable. This pressure, $P_{1,m}$ measured in volume V_I, is taken as the starting pressure of the binary mixture in the expansion run. Composition of the mixture is determined from the relation at constant temperature:

$$x_1 = \frac{n_1}{n_1 + n_2} = \frac{P_{o,1}V_I}{Z_{o,1}RT} \frac{Z_{1,m}RT}{P_{1,m}V_I} = \frac{P_{o,1}}{P_{1,m}} \frac{Z_{1,m}}{Z_{o,1}} \quad (4)$$

where n is the number of moles, x_1 the mole fraction of hydrocarbons, and $Z_{o,1}$ the compressibility factor of propane or propene corresponding to the pressure $P_{o,1}$. This value is known from prior measurements of the pure components. However, the compressibility factor of the mixture $Z_{1,m}$ (corresponding to pressure $P_{1,m}$) is determined by the Burnett method from experimental values of the same expansion run. Equation 4 can be generalized to n, component mixtures, if the masses of the first $(n - 1)$ pure substances are known:

$$x_i = \frac{n_i}{\sum\limits_{i=1}^{c} n_i} = \frac{P_{o,1}}{Z_{o,1}} \frac{Z_{1,m}}{P_{1,m}} \frac{n_i}{n_1} \quad (5)$$

where n_1 and n_i are known $(i \neq c)$.

Since the procedure requires repeated heating and freezing, the preparation of the mixture is tedious. The filling procedure of the Burnett chamber with hydrocarbons and helium and the experimental procedure require a cyclic operation in the temperature interval of about 173-424 K. The investigations of binary mixture for one composition at each temperature required six changes of the apparatus temperature during the entire filling procedure and preliminary determination of composition. Simultaneous with the temperature changes, the

Table II. Compressibility Factors, Virial Coefficients, and Apparatus Constants for the Propene–Helium System (atm = 101.325 kPa)

Run No. 7: $T = 393.20$ K, $x_I = 0.5608$, $B_I(T,x) = -37.33$ cm^3 mol^{-1}, $C_I(T,x) = 3606.3$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.57168$, $x_{II} = 0.5616$,
$B_{II}(T,x) = -36.26$ cm^3 mol^{-1}, $C_{II}(T,x) = 3210.7$ (cm^3)^2 mol^{-2}, $AN_{\infty II} = 1.57144$

r	P_r/atm	Z_{rI}	Z_{rII}	r	P_r/atm	Z_{rI}	Z_{rII}
1	61.6509	0.938 97		4	16.6028	0.981 42	0.981 88
2	40.0142	0.957 71	0.958 46	5	10.6332	0.987 95	0.988 26
3	25.8337	0.971 69	0.972 32	6	6.7963	0.992 24	0.992 45

Run No. 8: $T = 407.48$ K, $x_{II} = 0.5674$, $B_I(T,x) = -35.93$ cm^3 mol^{-1}, $C_I(T,x) = 4109.9$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.56677$,
$B_{II}(T,x) = -35.10$ cm^3 mol^{-1}, $C_{II}(T,x) = 3810.4$ (cm^3)^2 mol^{-2}, $AN_{\infty II} = 1.56660$

r	P_r/atm	Z_{rI}	Z_{rII}	r	P_r/atm	Z_{rI}	Z_{rII}
1	67.7788	0.941 70		5	11.8013	0.987 68	0.987 94
2	44.0330	0.958 38	0.958 97	6	7.5651	0.992 02	0.992 19
3	28.4964	0.971 64	0.972 15	7	4.8430	0.994 86	0.994 97
4	18.3669	0.981 17	0.981 54				

Run No. 9: $T = 407.50$ K, $x_{II} = 0.7131$, $B_I(T,x) = -74.06$ cm^3 mol^{-1}, $C_I(T,x) = 6774.0$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.56671$

r	P_r/atm	Z_{rI}	r	P_r/atm	Z_{rI}
1	60.7908	0.875 41	4	17.3763	0.961 97
2	40.5048	0.913 72	5	11.2438	0.975 27
3	26.6603	0.942 18			

Run No. 10: $T = 407.40$ K, $x_{II} = 0.5647$, $B_I(T,x) = -34.42$ cm^3 mol^{-1}, $C_I(T,x) = 3841.1$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.57218$,
$B_{II}(T,x) = -34.36$ cm^3 mol^{-1}, $C_{II}(T,x) = 3814.7$ (cm^3)^2 mol^{-2}, $AN_{\infty II} = 1.57217$

r	P_r/atm	Z_{rI}	Z_{rII}	r	P_r/atm	Z_{rI}	Z_{rII}
1	60.1491	0.948 52		5	10.2759	0.989 68	0.989 69
2	38.8900	0.964 05	0.964 09	6	6.5600	0.993 35	0.993 36
3	25.0411	0.975 84	0.975 87	7	4.1828	0.995 73	0.995 74
4	16.0631	0.984 11	0.984 13				

Run No. 11: $T = 423.03$ K, $x_{II} = 0.6521$, $B_I(T,x) = -48.56$ cm^3 mol^{-1}, $C_{II}(T,x) = 4570.7$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.57110$,
$B_{II}(T,x) = -51.81$ cm^3 mol^{-1}, $C_{II}(T,x) = 5930.2$ cm^3 mol^{-2}, $AN_{\infty II} = 1.57172$

r	P_r/atm	Z_{rI}	Z_{rII}	r	P_r/atm	Z_{rI}	Z_{rII}
1	61.1634	0.924 02		5	10.7082	0.985 24	0.984 34
2	30.9376	0.947 79	0.945 74	6	6.8514	0.990 51	0.989 90
3	25.8880	0.965 21	0.963 44	7	4.3753	0.993 91	0.993 52
4	16.6852	0.977 22	0.975 92				

Run No. 12: $T = 423.02$ K, $x_{II} = 0.8568$, $B_I(T,x) = -109.88$ cm^3 mol^{-1}, $C_{II}(T,x) = 9582.8$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.57093$

r	P_r/atm	Z_{rI}	r	P_r/atm	Z_{rI}
1	57.5836	0.816 27	5	11.1763	0.964 39
2	39.2473	0.873 87	6	7.2051	0.977 08
3	26.1895	0.915 99	7	4.6268	0.985 31
4	17.2001	0.945 02			

Run No. 13: $T = 423.01$ K, $x_{II} = 0.9311$, $B_I(T,x) = -135.51$ cm^3 mol^{-1}, $C_I(T,x) = 11\,442.9$ (cm^3)^2 mol^{-2}, $AN_{\infty I} = 1.57158$

r	P_r/atm	Z_{rI}	r	P_r/atm	Z_{rI}
1	60.5227	0.745 69	5	12.6420	0.949 72
2	42.5435	0.823 69	6	8.1932	0.967 62
3	28.9881	0.881 94	7	5.2774	0.979 23
4	19.2931	0.922 50			

pressure was changed from a vacuum of 5 × 10^{-4} Torr to 6865 kPa. Valves 1, 2, and 4 and the pressure indicator III were particularly exposed to significant pressure and temperature changes. Continuous and careful retightening of the apparatus was necessary for those reasons. Magnetic stirring was not applied and it was necessary to keep the mixture for at least 12 h at a temperature close to the investigated isotherm before the first expansion.

A somewhat simpler method was proposed by Hall and Eubank (4).

3. Results

To calculate the interaction second virial coefficients of binary mixtures it is more convenient to know the virial coefficient of the mixture determined under the same conditions as for the pure substances. Our results for pure helium, obtained in the same apparatus and for the temperature range 373–423 K, are described elsewhere (8). Also, calculated results for propane,

propene, and their mixtures are in press (9).

To avoid large adsorption effects in the Burnett apparatus, the mixtures have not been investigated at temperatures lower than some 20–30 K above the critical temperatures of the hydrocarbons. The compressibility factors plus the second and the third virial coefficients of the given mixtures have been calculated for six propane + helium mixtures (runs 1–6) and for seven propene + helium mixtures (runs 7–13) at three temperatures equal to about 393.15, 408.15, and 423.15 K. The experimental and calculated values of P/RT were minimized by the least-squares method (10). The calculation method has been checked and tested by the data of Canfield et al. (2). The results of the calculations are given in Tables I and II. Two values of the virial coefficients and apparatus constants for each expansion run result from calculation of a full pressure set and a second set without the starting pressure. The first set is indicated by I and the second by II or b. The elimination of the first pressure allows an estimation of the internal consistency of the measurements. The divergence of the results may follow

Table III. Mean Second Virial Coefficients of Helium (8), $B_{22}(T)$

T/K	$B_{22}(T)/\text{cm}^3\ \text{mol}^{-1}$
393.2	$^1/_3$(11.36 + 11.34 + 11.30) = 11.33
407.5	$^1/_4$(11.24 + 11.22 + 11.18 + 11.42) = 11.26
423.0	11.13

from truncating $D(T)$ in virial expansion and, possibly, from adsorption effects occurring in the Burnett apparatus. Most probably, the maximum pressure is beyond the range of the truncated virial equation. As pointed out by Eubank and Angus (3) the use of a least-squares criterion with a truncated virial expansion provides another source of uncertainty in B, C, and AN_∞. Also, the low pressure capability of the apparatus was only 3-4 atm. For these reasons, the fitted values of AN_∞ for both our cells were somewhat dependent on the composition and the inclusion of the starting pressure.

The interaction or cross second virial coefficients B_{12} were determined from the equation

$$B_{12}(T) = \frac{1}{2x_1 x_2}[B(T,x) - x_1^2 B_{11}(T) - x_2^2 B_{22}(T)] \quad (6)$$

where subscript 1 refers to propane or propene, $B_{12}(T)$ is the cross second virial coefficient, $B(T,x)$ is the second virial coefficient of the mixture and x_2 is the mole fraction of helium. For $B_{22}(T)$ values we used our own data for pure helium (8) taking the arithmetic mean of B_{22} for a given isotherm. The mean second virial coefficients are listed in Table III. Since the composition has been determined indirectly from eq 4, two values are given. The calculations of the interaction second virial coefficients were performed in two variants, i.e., from the pressure set in expansion run and by omitting the starting pressure and employing consistently the same variant for mixtures and pure substances. The values of the second virial coefficients of pure substances (in press) and second virial coefficients of mixtures and cross second virial coefficients for both binary systems are presented in Tables IV and V. Several

Table IV. Interaction Second Virial Coefficients for the Propane-Helium System

No. of expansion run	T/K	Molar fraction, x	Mixture of second virial coeff, $B(T,x)/\text{cm}^3\ \text{mol}^{-1}$	Second virial coeff of propane, $B_{11}(T)/\text{cm}^3\ \text{mol}^{-1}$	Second virial coeff of helium, $B_{22}(T)/\text{cm}^3\ \text{mol}^{-1}$	Interaction of second virial coeff, $B_{12}(T)/\text{cm}^3\ \text{mol}^{-1}$
1	393.18	0.7672	−111.85 −111.18[b]	−212.31 −214.76[b]	11.33	34.98 (40.90[b])
		0.7696[a]	−111.85 −111.18[b]	−212.31 −214.7[b]		(37.53) 43.5[b,c]
2	393.19	0.7063 0.7084[a]	−87.88 −87.88	−212.31 −212.31	11.33	41.11 (42.86[c])
3	407.49	0.6255	−56.10 −58.74[b]	−194.69 −198.19[b]	11.26	39.48 (36.77[b])
		0.6273[a]	−56.10 −58.74[b]	−194.69 −198.19[b]		(40.53) 37.83[b,c]
4	407.40	0.4224	−12.09 −10.23[b]	−194.69 −198.19[b]	11.26	38.72 (43.81[b])
		0.4232[a]	−12.09 −10.23[b]	−194.69 −198.19[b]		(38.96) 44.08[b,c]
5	423.00	0.3914	−4.07 −2.40[b]	−179.91 −181.29[b]	11.13	40.75 (44.70[b])
		0.3918[a]	−4.07 −2.40[b]	−179.91 −181.29[b]		(40.87) 44.82[b,c]
6	423.00	0.8080[a]	−104.88 −104.71[b]	−179.91 −181.29[b]	11.13	(39.18) 42.63[b,c]

[a] Composition estimated by eq 4 when starting run pressure omitted in data analysis of pure hydrocarbons. [b] Virial coefficient values calculated without starting pressure. [c] Probably best values.

Table V. Interaction Second Virial Coefficients for the Propene + Helium System

No. of expansion run	T/K	Molar fraction, x	Mixture of second virial coeff, $B(T,x)/\text{cm}^3\ \text{mol}^{-1}$	Second virial coeff of propene, $B_{11}(T)/\text{cm}^3\ \text{mol}^{-1}$	Second virial coeff of helium, $B_{22}(T)/\text{cm}^3\ \text{mol}^{-1}$	Interaction of second virial coeff, $B_{12}(T)/\text{cm}^3\ \text{mol}^{-1}$
7	393.20	0.5608	−37.33 −36.26[b]	−189.15 −190.98[b]	11.33	40.53 (43.87[b])
		0.5616[a]	−37.33 −36.26[b]	−189.15 −190.98[b]		(40.94) 44.22[b,c]
8	407.48	0.5674[a]	−35.93 −35.10[b]	−174.73 −176.25[b]	11.26	(37.10) 39.79[b,c]
9	407.50	0.7131[a]	−74.06	−174.73 −176.25[b]	11.26	(33.87) 35.76[b,c]
10	407.40	0.5647[a]	−34.42 −34.36[b]	−174.73 −176.25[b]	11.26	(38.98) 40.09[b,c]
11	423.03	0.6521[a]	−48.56 −51.81[b]	−161.05 −162.22[b]	11.13	(40.98) 34.92[b,c]
12	423.02	0.8568[a]	−109.88	−161.05 −162.22[b]	11.13	(33.19) 36.60[b,c]
13	423.01	0.9311[a]	−135.51	−161.05 −162.22[b]	11.13	(31.69) 39.60[b,c]

[a] Composition estimated by eq 4 when starting run, pressure omitted in data analysis of pure hydrocarbons. [b] Virial coefficient values calculated without starting pressure. [c] Probably best values.

ways to calculate B_{12} are possible; most points were calculated by using all pressures.

The errors must be related to direct measurement of temperature, pressure, and composition of mixture. The probable error in pressure measurements does not exceed $\pm 0.02\%$ at any pressure. The source of error in pressure are weight calibration, effective area of the piston and cylinder of the dead weight gauge, barometric pressure, hydraulic head correction, and the reading and "null" correction of the differential pressure indicator, as discussed in detail earlier (7–9). The temperature was kept constant to within less than 0.01 K. If long time drifts occurred during several hours of continuous operation of the thermostating bath, the pressures were corrected and all brought to the same temperature for the given expansion run. The resulting pressure error is far below the accuracy stated above and the error in temperature is estimated at ± 0.01 K.

4. Discussion

The values of $B(T)$ and $C(T)$ for pure substances are in very good agreement (7, 9) with literature data. Thus, the accuracy of $B(T,x)$ determination should be also satisfactory. An additional error arises, however, from indirect determination of composition by means of eq 4. The excess virial coefficients of binary mixtures ($2B_{12} - B_{11} - B_{22}$) are very high, being of the order of $+280$ cm^3 mol^{-1}. This deviation is higher than the value of either virial coefficient of the pure components. The derived values of $B_{12}(T)$ are consistent with the accuracy of ± 4 cm^3 mol^{-1}. For the propane + helium system, $B_{12}(T)$ increases but slightly with temperature. This suggests that $B_{12}(T)$ is located, in the neighborhood of the maximum and is confirmed by a qualitative discussion based on the Lennard–Jones (6–12) potential. Application of the Lennard–Jones (6–12) potential with the pure component values of σ and ϵ taken from Hirschfelder et al. (5), i.e., $\epsilon/k = 6.03$ K and $\sigma = 2.63$ Å for helium, $\epsilon/k = 242$ K and $\sigma = 5.637$ Å for propane, yields the geometric mean $\epsilon_{12}/k = 38.2$ and arithmetical mean $\sigma_{12} = 4.133$ Å. These values predict $B_{12}(T)$ from 41.2 to 41.6 cm^3/mol^{-1} for T from 393.2 to 423.0 K—in fair agreement with our data from Table IV. The force parameters estimated from the pure component

data (9) are $\epsilon/k = 4.65$ K and $\sigma = 2.662$ Å for He, $\epsilon/k = 225$ K and $\sigma = 5.811$ Å for propane, and $\epsilon/k = 240$ K and $\sigma = 5.34$ Å for propene. These values produce for the helium–propane system $B_{12}(T)$ equal to 45.5–46.1 cm^3 mol^{-1} and for helium–propene 38.1–38.6 cm^3 mol^{-1} for the same temperature range. The agreement with the mixture data is as good as can be expected as the Lennard–Jones potential was developed for spherical molecules. Moreover, large differences in size between helium and the hydrocarbon compounds require potential functions which would take this into account besides the orientational effects.

Unfortunately, our data reported here for B_{12} extend only from 398 to 423 K and any analysis in terms of intermolecular potential functions is thus prohibited. Therefore we have refrained from any fitting procedures; the above calculations are meant to show an order-of-magnitude agreement.

We hope to consider in future papers the details of the hydrocarbon–helium interaction in the context of the $B_{12}(T)$ values using all possible data, along with our data reported here, so as to extend as much as possible the temperature range and the range of molecular volume of the larger component.

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Refractive Index of Molten Lewis Acid Salt Hydrates: Mixtures of Cr(NO₃)₃·9H₂O + Ca(NO₃)₂·4H₂O

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Refractive indices of molten $Cr(NO_3)_3 \cdot 9H_2O$ + $Ca(NO_3)_2 \cdot 4H_2O$ mixtures have been measured as a function of temperature and composition. Refractive index–composition (in mol % of $Ca(NO_3)_2 \cdot 4H_2O$) isotherms showed a "break" at ≈ 39 mol % of divalent ion salt hydrate. Molar polarizations, computed using the Lorenz–Lorentz equation, varied linearly with composition. Expansivities calculated from temperature coefficient of refractive index were found to be much smaller than those obtained from density measurements.

Volumetric, surface, and flow properties of $Ca(NO_3)_2 \cdot 4H_2O$ and $Cd(NO_3)_2 \cdot 4H_2O$ and a number of Lewis acid salt hydrates

of metals belonging to 3d series of transition elements in pure (3, 5) and mixed (2, 4, 6) states have recently been reported. In an effort to gather more evidence for the existence of hydration–dehydration tendencies in mixed melts, refractive index measurements on the system $Cr(NO_3)_3 \cdot 9H_2O$ + $Ca(NO_3)_2 \cdot 4H_2O$ are reported in this paper.

Experimental Section

Material. $Ca(NO_3)_2 \cdot 4H_2O$ (BDH, India) and $Cr(NO_3)_3 \cdot 9H_2O$ (Ortanal, Italy) were of analytical reagent grade. The melting temperatures of these salts as determined by the cooling curve method were found to be 42.5 and 36.8 °C, the corresponding literature liquidus temperatures being 42.7 and 37 °C, re-