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# Thermodynamics of binary liquid mixtures of partially deuterated methanes with CH<sub>4</sub> or CD<sub>4</sub>

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The vapor pressure isotope effect of samples of isotopically substituted methane and their mixtures was measured as a function of temperature and mixture composition: The differential vapor pressure between CH<sub>i</sub>D<sub>4-i</sub> (with  $i=0$  or 4) and CH<sub>j</sub>D<sub>4-j</sub> (with  $j=1, 2$ , or 3), the differential vapor pressure between mixtures of (CH<sub>i</sub>D<sub>4-i</sub>+CH<sub>j</sub>D<sub>4-j</sub>) and CH<sub>4</sub> (if  $i=4$ ) or CH<sub>j</sub>D<sub>4-j</sub> (if  $i=0$ ) and the absolute vapor pressure of CH<sub>4</sub> (if  $i=4$ ) or CH<sub>j</sub>D<sub>4-j</sub> (if  $i=0$ ), were measured simultaneously between 96 and 121 K for mixtures of nominal composition 0.25, 0.50, and 0.75 mole fraction in the reference methane species. The  $p(x,T)$  data were used to calculate the excess molar Gibbs energy function,  $G^E(x,T)$  and the excess molar enthalpy  $H^E(x)$ , assuming that this last function is independent of temperature in the experimental range. The deviations from ideal behavior are very small,  $G^E$  being only some tenths of J/mol for equimolar mixtures. The experimental  $G^E$  values compare well with estimated results based on a modified version of the statistical theory of isotope effects in condensed phases. Comparisons with reported values of the liquid-vapor isotope fractionation factor for the CD<sub>3</sub>H-CH<sub>4</sub> system are also made. © 1997 American Institute of Physics. [S0021-9606(97)50621-0]

## I. INTRODUCTION

In a previous paper<sup>1</sup> we reported on the vapor pressure isotope effects (VPIE) in mixtures of (CH<sub>4</sub>+CD<sub>4</sub>). Several statistical theories of liquid mixtures were tested: The van der Waals (VDW) one-fluid theory, a one-center Lennard-Jones (LJ) perturbation theory as well as the theory of isotope effects. The results were best interpreted in terms of contributions from each molecular motion (internal vibration, hindered translation, or liberation) to the overall effect, within the framework of the theory of isotope effects in mixtures.<sup>2-5</sup> A way to take this analysis one step further is to consider systems of partially deuterated methane molecules (CH<sub>3</sub>D, CH<sub>2</sub>D<sub>2</sub>, and CHD<sub>3</sub>), where the relative magnitude of those contributions (internal and external) is shifted due to changes in the moment of inertia, reduced mass, center-of-mass, and general symmetry of the molecules.

The VPIE between partially deuterated methane molecules and CH<sub>4</sub> was first determined experimentally by Armstrong *et al.*<sup>6</sup> and interpreted theoretically by Bigeleisen *et al.*<sup>7</sup> and Pollin and Ishida.<sup>8,9</sup> These results were recently confirmed by Calado *et al.*<sup>10</sup> who also measured the VPIE between the partially deuterated methanes and CD<sub>4</sub>. These data will constitute the basis for the experimental and theoretical extension to mixtures reported in this paper.

The VPIE in mixtures containing partially deuterated methane molecules will be analyzed through the calculation of thermodynamic excess properties, namely the excess molar Gibbs energy,  $G^E$ , and the excess molar enthalpy,  $H^E$ ,

both determined from experimental vapor pressure data.

The aim of the present work is to report on the experimental vapor pressure data as well as to interpret the results using the theory of isotope effects in mixtures, and thus, to complement the previous study on (CH<sub>4</sub>+CD<sub>4</sub>) mixtures. For the particular case of the (CD<sub>3</sub>H+CH<sub>4</sub>) system there are two ways of assessing its nonideality, since both VPIE and liquid-vapor isotope fractionation factors (LVIFF) are available;<sup>11</sup> the two estimated values of  $G^E$  are compared.

## II. EXPERIMENT

All methane species were taken from samples which were used and analyzed in previous works.<sup>1,10,12</sup> and where the isotopic composition of each sample is known. The vapor pressure data were measured using a doubly differential manometric technique described elsewhere.<sup>12</sup>

For a given system, each of the three cells of the cryostat were filled to 1/3 of its (volumetric) capacity with CH<sub>i</sub>D<sub>4-i</sub> (with  $i=0$  or 4), CH<sub>j</sub>D<sub>4-j</sub> (with  $j=1, 2$ , or 3) and the mixture (CH<sub>i</sub>D<sub>4-i</sub>+CH<sub>j</sub>D<sub>4-j</sub>), respectively. The liquid-vapor equilibrium of the samples was monitored by measuring the different vapor pressure between the two pure samples, the differential vapor pressure between the mixture and the reference sample, and the absolute vapor pressure of the reference sample (CH<sub>4</sub> if  $i=4$  or CH<sub>j</sub>D<sub>4-j</sub> if  $i=0$ ). Differential pressures were measured using two differential capacitance manometers (Datametrix model 572) with 100 Torr ( $\approx 13$  kPa) range and 0.13 Pa resolution. Absolute pressures were read by a differential capacitance manometer (Datametrix model 570) with 100 in Hg ( $\approx 340$  kPa) range and 3.4 resolution and a fused quartz bourdon gauge (Texas Instruments model 145) with 60 psi ( $\approx 415$  kPa) range and 4.1 Pa resolution.

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The temperature of the cryostat was maintained within the chosen temperature range using liquid nitrogen as cooling agent and electrical resistance coils for heating, which are wound around an evacuated adiabatic shield. During the acquisition of each experimental datum point the temperature was kept within 0.01 K (or less) for periods of over half an hour after complete stabilization of the pressure readings. Temperature readings were made in the IPT-90 scale with an estimated accuracy of 0.01 K, using a four-wire resistance thermometer connected to an integrating digital multimeter (PREMA 6031), with 0.001 K resolution. Using doubly differential manometry for the observation of vapor pressures with the three cells filled with the same liquid sample, we estimated that temperature differences between the three cells are less than  $10^{-4}$  K.

The overall composition of the mixture,  $X_T$ , was determined by simple manometry with an accuracy of 0.05%.

### III. RESULTS

For each system, the absolute vapor pressure of the reference species,  $p_a^0$ , the differential vapor pressure between the two pure component samples,  $\Delta p_{(b-a)}^0$ , and the differential vapor pressure between the mixture and the reference species,  $\Delta p_{(m-a)}^0$ , are presented in Table I. 90  $p$ - $X_T$ - $T$  data points in the 96–121 K temperature range are recorded, corresponding to 18 mixtures with total composition,  $X_T$ , of  $\sim 0.25$ , 0.50, or 0.75 mol fraction in the reference species.

The zero-pressure excess molar Gibbs energy function,  $G^E(x, T)$ , for a given temperature and liquid phase composition,  $x_a$ , was calculated from the  $p$ - $X_T$ - $T$  data presented in Table I using the method of Calado.<sup>13,14</sup> In order to perform these calculations one has to know several physical properties (such as molar volumes, second virial coefficients, and isothermal compressibility coefficients) of the partially deuterated methanes. The literature sources or, when lacking, the methodology followed to estimate them was previously described in detail.<sup>1</sup> Values of  $G^E$  are also shown in Table I along with the calculated values of liquid and gas phase composition,  $x_a$  and  $y_a$ , respectively, as well as the activity coefficient,  $\gamma_a$ , of the reference species. Values for the excess pressure  $p^E$ , defined as

$$p^E = \Delta p_{(m-a)}^0 - (1 - x_a)\Delta p_{(b-a)}^0, \quad (1)$$

are also included.

Considering that in the experimental temperature range covered in this study, both  $H^E$  and  $S^E$  are independent of temperature,  $G^E = H^E - TS^E$  and that given the similarity of the two isotopic species the excess functions can be approximated to a one-term Redlich–Kister expansion

$$G^E/RT = (A + B/T)x_ax_b; \quad H^E/R = Bx_ax_b. \quad (2)$$

For each system the  $A$  and  $B$  parameters are presented in Table II along with the standard and maximum deviations of the fit. In Figs. 1(a)–1(f), two cross sections at constant temperature (100 and 120 K) of the fitted surfaces are shown, the results obtained being compared with those found for the ( $\text{CH}_4 + \text{CD}_4$ ) system.<sup>1</sup> The points in Figs. 1(a) and 1(b) represent

values of  $G^E$  taken from each experimental run (mixture), interpolated for the selected temperatures. Likewise, the fitting curves for  $H^E$  are shown in Figs. 2(a)–2(f).

Both  $G^E$  and  $H^E$  are positive (as well as  $S^E$ ). These deviations from ideality in the liquid represent more than 90% of the total deviation from Raoult's law, while the remaining 10% are due to gas imperfection.

In the case of the  $\text{CH}_4 + \text{CH}_3\text{D}$  system, where a crossover in the vapor pressure of the pure components occurs at 99.76 K, the observation of a positive excess pressure implies the occurrence of an azeotrope at that particular temperature. Such behavior is depicted in Fig. 3, where a modified  $p$ - $x_a$ - $y_a$  diagram (cf. figure caption) is presented.

### IV. DISCUSSION

Deviations from ideality in isotopic mixtures are inevitably very small since structural and energetical differences among the constituents of the solution are strongly minimized. Previous studies on this kind of systems<sup>1,4,5</sup> have shown that the most commonly used theories for liquid mixtures, such as the van der Waals one-fluid theory or perturbation theories (which take into account shape and/or polarity) do not prove to be very successful. Vibrational effects and their density dependence, which are neglected in this type of theories, are strongly enhanced in isotopic mixtures, and thus represent the major contribution to their nonideal behavior. Therefore, the results presented in the last section will be discussed considering the theory of isotope effects in mixtures.<sup>2–5</sup> In the case of the ( $\text{CH}_4 + \text{CD}_4$ ) system,<sup>1</sup> this theory proved to be the most adequate way of estimating the deviations from ideality.

#### A. Theoretical interpretation

The theory developed by Jancsó and Van Hook within the framework of the pseudoharmonic oscillator,<sup>2,3</sup> is based on the concepts established in the statistical theory of isotope effects in condensed phases proposed by Bigeleisen.<sup>15</sup> It was originally developed to predict activity coefficients at infinite dilution of one isotopically substituted molecule in the other, and later extrapolated to include finite concentrations. In its simplest form the excess molar Gibbs energy is given by

$$G^E = RT \frac{\Delta V}{\langle V \rangle} x_a x_b \left[ \frac{1}{2} \sum_{i=1}^{3N-6} (x_b \Gamma_{ai} u_{ai} + x_a \Gamma_{bi} u_{bi}) + \frac{1}{12} \sum_{i=1}^6 (x_b \Gamma_{ai} u_{ai}^2 + x_a \Gamma_{bi} u_{bi}^2) \right], \quad (3)$$

where  $\Delta V$  is the difference between the orthobaric molar volumes of the two molecules,  $a$  and  $b$ ,  $\langle V \rangle$  is the average molar volume between the two species,  $\Gamma_i$  is the Grüneisen parameter corresponding to the  $i$ th mode of molecular motion and  $u_i = h \nu_i / kT$ , where  $h$  is the Planck constant,  $\nu_i$  the frequency of the  $i$ th normal mode of vibration and  $k$  the Boltzmann constant. The Grüneisen parameter,  $\Gamma_i$  is defined as  $\Gamma_i = -(\partial \ln \nu_i / \partial \ln V)_T$ . Equation (3) shows that the excess thermodynamic property  $G^E$  can be predicted on the basis of the molar volume isotope effect (MVIE), the set of

TABLE I. Experimental and calculated data as a function of temperature  $T$  and mixture composition (total mol fraction of the reference nuclide  $a$ ),  $X_{Ta}$ : Absolute vapor pressure of the reference species,  $p_a^0$ , differential vapor pressure between the pure components of the mixture,  $\Delta p_{(b-a)}^0$ , and between the mixture and the reference species,  $\Delta p_{(m-a)}^0$ , excess pressure,  $p^E$ , defined by Eq. (1), liquid and gas phase composition of the mixture (mole fraction of the reference species),  $x_a$  and  $y_a$ , respectively, activity coefficient of the reference species in the liquid phase,  $\gamma_a$ , and excess molar Gibbs energy,  $G^E$ .

$X_{Ta}$	$T$ (K)	$p_a^0$ (kPa)	$\Delta p_{(b-a)}^0$ (kPa)	$\Delta p_{(m-a)}^0$ (kPa)	$p^E$ (kPa)	$x_a$	$y_a$	$10^3 \times \ln \gamma_a$	$G^E$ (J/mol)
CH <sub>4</sub> +CH <sub>3</sub> D ( $a+b$ )									
0.5002	97.72	26.961	-0.0175	-0.0043	0.0045	0.5002	0.5003	0.162	0.132
	105.40	58.549	0.0976	0.0568	0.0080	0.5002	0.4998	0.134	0.117
	110.93	95.518	0.2961	0.1595	0.0115	0.5002	0.4995	0.115	0.106
	115.61	138.75	0.5317	0.2798	0.0141	0.5002	0.4993	0.097	0.093
	118.09	166.96	0.7141	0.3721	0.0152	0.5003	0.4993	0.085	0.084
0.4999	98.23	28.488	-0.0147	-0.0027	0.0047	0.4999	0.5001	0.161	0.132
	101.78	41.247	0.0241	0.0183	0.0062	0.4999	0.4998	0.146	0.124
	108.11	74.898	0.1704	0.0951	0.0099	0.5000	0.4994	0.127	0.114
	112.54	108.811	0.3586	0.1913	0.0120	0.5000	0.4992	0.107	0.099
	118.43	171.13	0.7573	0.3957	0.0171	0.5000	0.4990	0.093	0.092
CH <sub>4</sub> +CH <sub>2</sub> D <sub>2</sub> ( $a+b$ )									
0.4993	98.89	30.674	0.1685	0.0925	0.0082	0.4994	0.4980	0.263	0.215
	103.59	49.339	0.3903	0.2073	0.0119	0.4994	0.4975	0.235	0.202
	107.93	73.721	0.6986	0.3650	0.0154	0.4995	0.4972	0.200	0.180
	113.94	121.700	1.4079	0.7252	0.0207	0.4996	0.4969	0.163	0.154
	119.41	183.44	2.2657	1.1606	0.0274	0.4998	0.4970	0.139	0.139
0.5000	102.48	44.267	0.3187	0.1715	0.0121	0.5000	0.4983	0.267	0.227
	106.66	65.757	0.5915	0.3120	0.0163	0.5000	0.4979	0.239	0.212
	111.27	98.079	1.0343	0.5373	0.0203	0.5001	0.4976	0.198	0.183
	115.83	140.95	1.6721	0.8599	0.0241	0.5002	0.4974	0.162	0.156
	119.87	189.80	2.4006	1.2280	0.0283	0.5002	0.4973	0.139	0.139
0.7500	97.83	27.304	0.1465	0.0421	0.0055	0.7500	0.7490	0.066	0.161
	107.81	72.887	0.6969	0.1873	0.0132	0.7501	0.7483	0.058	0.156
	111.86	102.979	1.1081	0.2938	0.0170	0.7501	0.7481	0.052	0.146
	115.80	140.70	1.6668	0.4350	0.0186	0.7502	0.7480	0.041	0.120
	120.35	196.57	2.5142	0.6515	0.0236	0.7502	0.7479	0.037	0.112
0.2495	99.54	32.832	0.2005	0.1568	0.0063	0.2495	0.2485	0.564	0.155
	106.80	66.622	0.6057	0.4662	0.0117	0.2496	0.2480	0.513	0.151
	111.77	102.233	1.0930	0.8359	0.0157	0.2496	0.2478	0.443	0.137
	116.04	143.26	1.7120	1.3036	0.0191	0.2497	0.2476	0.380	0.122
	119.78	188.60	2.3680	1.7995	0.0228	0.2497	0.2476	0.340	0.113
CH <sub>4</sub> +CHD <sub>3</sub> ( $a+b$ )									
0.4998	98.85	30.457	0.3584	0.1923	0.0131	0.5000	0.4971	0.419	0.344
	103.94	51.018	0.7474	0.3924	0.0187	0.5000	0.4965	0.354	0.306
	108.30	76.170	1.2694	0.6594	0.0248	0.5001	0.4961	0.313	0.282
	112.35	107.218	1.9544	1.0088	0.0319	0.5001	0.4958	0.283	0.265
	115.89	141.60	2.7436	1.4102	0.0389	0.5002	0.4957	0.261	0.251
0.4999	119.49	184.70	3.7654	1.9289	0.0475	0.5003	0.4956	0.240	0.239
	98.92	30.660	0.3738	0.1995	0.0125	0.4998	0.4968	0.397	0.326
	102.25	43.232	0.6071	0.3190	0.0154	0.4998	0.4964	0.344	0.293
	105.78	60.635	0.9563	0.4976	0.0193	0.4999	0.4961	0.307	0.270
	108.95	80.545	1.3774	0.7121	0.0233	0.4999	0.4958	0.277	0.251
0.7501	112.52	108.676	2.0018	1.0302	0.0293	0.5000	0.4956	0.256	0.240
	115.96	142.41	2.7776	1.4243	0.0357	0.5001	0.4955	0.238	0.229
	120.36	196.36	4.0613	2.0752	0.0454	0.5002	0.4954	0.217	0.217
	101.27	39.245	0.5065	0.1376	0.0110	0.7501	0.7476	0.091	0.230
	105.58	59.567	0.9063	0.2414	0.0150	0.7502	0.7473	0.081	0.212
0.2504	110.07	88.736	1.5268	0.4014	0.0201	0.7502	0.7470	0.071	0.197
	116.13	144.34	2.7919	0.7261	0.0290	0.7503	0.7468	0.063	0.183
	119.81	188.94	3.8509	0.9943	0.0332	0.7504	0.7468	0.006	0.127
	99.95	34.054	0.4493	0.3448	0.0080	0.2504	0.2481	0.687	0.191
	105.67	59.940	0.9558	0.7270	0.0106	0.2505	0.2477	0.516	0.151
CH <sub>3</sub> D+CD <sub>4</sub> ( $a+b$ )	111.15	96.756	1.7480	1.3254	0.0153	0.2505	0.2474	0.452	0.140
	116.84	151.36	3.0011	2.2699	0.0211	0.2506	0.2472	0.394	0.128
	120.23	193.99	4.0169	3.0359	0.0261	0.2507	0.2472	0.378	0.127
	96.04	22.278	0.4161	0.2200	0.0121	0.5003	0.4958	0.530	0.423
	101.21	38.974	0.8279	0.4324	0.0187	0.5004	0.4952	0.465	0.392
0.5003	106.74	66.419	1.5496	0.8025	0.0284	0.5004	0.4949	0.411	0.365
	112.48	111.524	2.7416	1.4094	0.0401	0.5006	0.4948	0.343	0.321
	117.93	165.71	4.3271	2.2134	0.0531	0.5007	0.4947	0.302	0.297

TABLE I. (Continued).

$X_{Ta}$	$T$ (K)	$p_a^0$ (kPa)	$\Delta p_{(b-a)}^0$ (kPa)	$\Delta p_{(m-a)}^0$ (kPa)	$p^E$ (kPa)	$x_a$	$y_a$	$10^3 \times \ln \gamma_a$	$G^E$ (J/mol)
0.7514	101.16	38.770	0.8297	0.2193	0.0132	0.7515	0.7475	0.109	0.276
	105.86	61.263	1.4241	0.3730	0.0192	0.7516	0.7473	0.100	0.265
	110.23	90.194	2.2068	0.5738	0.0257	0.7516	0.7471	0.089	0.249
	114.72	130.140	3.3347	0.8611	0.0332	0.7517	0.7471	0.079	0.230
	119.36	183.92	4.8721	1.2499	0.0408	0.7518	0.7471	0.069	0.207
0.2507	97.66	26.758	0.5210	0.4002	0.0099	0.2508	0.2474	1.082	0.294
	105.10	57.070	1.3090	0.9982	0.0176	0.2508	0.2469	0.892	0.261
	110.23	90.126	2.2097	1.6803	0.0250	0.2509	0.2467	0.797	0.245
	114.94	132.141	3.3759	2.5625	0.0340	0.2510	0.2466	0.735	0.235
	120.01	192.43	5.0816	3.8473	0.0419	0.2511	0.2467	0.616	0.206
CH <sub>2</sub> D <sub>2</sub> +CD <sub>4</sub> ( $a+b$ )									
0.4999	101.28	39.635	0.5975	0.3128	0.0140	0.5000	0.4963	0.342	0.289
	107.00	68.471	1.1251	0.5830	0.0205	0.5001	0.4961	0.289	0.257
	111.82	103.694	1.7990	0.9259	0.0267	0.5001	0.4960	0.247	0.229
	115.84	142.68	2.5510	1.3058	0.0308	0.5002	0.4960	0.204	0.197
	119.20	182.97	3.3504	1.7097	0.0355	0.5003	0.4960	0.182	0.181
0.2501	100.83	37.837	0.5535	0.4257	0.0107	0.2502	0.2477	0.826	0.231
	107.41	71.072	1.1757	0.8977	0.0162	0.2502	0.2474	0.660	0.197
	114.06	124.274	2.1896	1.6649	0.0235	0.2503	0.2473	0.541	0.171
	119.18	182.81	3.3582	2.5471	0.0299	0.2504	0.2473	0.461	0.153
	101.43	40.097	0.5957	0.1593	0.0106	0.7503	0.7474	0.085	0.215
0.7502	106.54	65.679	1.0687	0.2828	0.0159	0.7503	0.7473	0.078	0.207
	113.21	116.139	2.0404	0.5309	0.0216	0.7504	0.7472	0.059	0.167
	118.57	174.90	3.1751	0.8189	0.0268	0.7505	0.7473	0.048	0.142
CHD <sub>3</sub> +CD <sub>4</sub> ( $a+b$ )									
0.5000	100.30	35.920	0.3385	0.1771	0.0078	0.5000	0.4977	0.213	0.177
	105.65	60.856	0.6195	0.3218	0.0120	0.5001	0.4976	0.191	0.168
	111.19	99.113	1.0553	0.5438	0.0163	0.5001	0.4976	0.158	0.146
	116.15	147.23	1.6021	0.8195	0.0187	0.5002	0.4976	0.121	0.117
	120.40	201.01	2.2128	1.1267	0.0208	0.5002	0.4977	0.099	0.098
0.4963	0.102.93	46.947	0.4625	0.2345	0.0016	0.4963	0.4939	0.033	0.028a
	108.95	81.902	0.8586	0.4366	0.0042	0.4964	0.4939	0.050	0.045a
	113.53	120.103	1.2928	0.6666	0.0156	0.4964	0.4939	0.126	0.117
	118.09	170.42	1.8660	0.9577	0.0181	0.4965	0.4939	0.103	0.099

spectroscopic data that enables the description of the VPIE and their mutual relation (Grüneisen parameter). All these data are to be measured or calculated for the pure components of the mixture only: The theory handles mixtures without the use of any *ad hoc* mixing or combination rule.

Molar volume isotope effect (MVIE) data can be found in the literature for the (CH<sub>4</sub>+CD<sub>4</sub>) pair.<sup>16,17</sup> The MVIE data necessary for the systems studied in this work were estimated assuming the validity of the arithmetic mean rule for the molar volumes of the partially deuterated methane molecules. This approximation is quite reasonable considering: (i) The small MVIE between methane species (in this case the geometrical and arithmetic mean rule give approximately the same results), and (ii) the fact that through Eq. (3)  $G^E$  will be scaled up by  $\Delta V$  in a linear way, i.e., even if there are small deviations to the arithmetic mean rule, those will probably be negligible as compared with the uncertainty associated with the estimates of other parameters.

A set of frequencies for each species was calculated by Bigeleisen *et al.* These results were obtained considering the harmonic oscillator approximation and represent a coherent set of data values that describes correctly the VPIE between the pure methane species.

The Grüneisen parameters,  $\Gamma_i$ , corresponding to each frequency can be calculated from the knowledge of density and spectroscopic experimental data along isotherm curves or, alternatively, using the shifts in density and frequency occurring at the triple point as suggested by Calado *et al.*<sup>1</sup> and Rebelo.<sup>18</sup> The former method is the most direct and correct, but generally not all the necessary data are available. Furthermore, the internal coherence of the set of spectroscopical data fitted to the VPIE is not taken into account if the Grüneisen parameter is calculated using experimental data from different sources. The approximate method based

TABLE II. Fitting parameters,  $A$  and  $B$ , of Eq. (2). The standard deviation,  $\sigma_{\text{std.}}$ , of each fit is also given.

Mixture	$A \times 10^3$	$B/K$	$\sigma_{\text{std.}}$
CH <sub>4</sub> +CH <sub>3</sub> D	$-1.047 \pm 0.055$	$0.1664 \pm 0.0059$	2.7
CH <sub>4</sub> +CH <sub>3</sub> D <sub>2</sub>	$-1.765 \pm 0.173$	$0.2819 \pm 0.0189$	5.6
CH <sub>4</sub> +CHD <sub>3</sub>	$-2.388 \pm 0.408$	$0.3864 \pm 0.0445$	4.4
CH <sub>3</sub> D+CD <sub>4</sub>	$-2.709 \pm 0.155$	$0.4592 \pm 0.0167$	2.4
CH <sub>2</sub> D <sub>2</sub> +CD <sub>4</sub>	$-2.899 \pm 0.170$	$0.4353 \pm 0.0187$	3.5
CHD <sub>3</sub> +CD <sub>4</sub>	$-1.954 \pm 0.216$	$0.2842 \pm 0.0238$	6.1

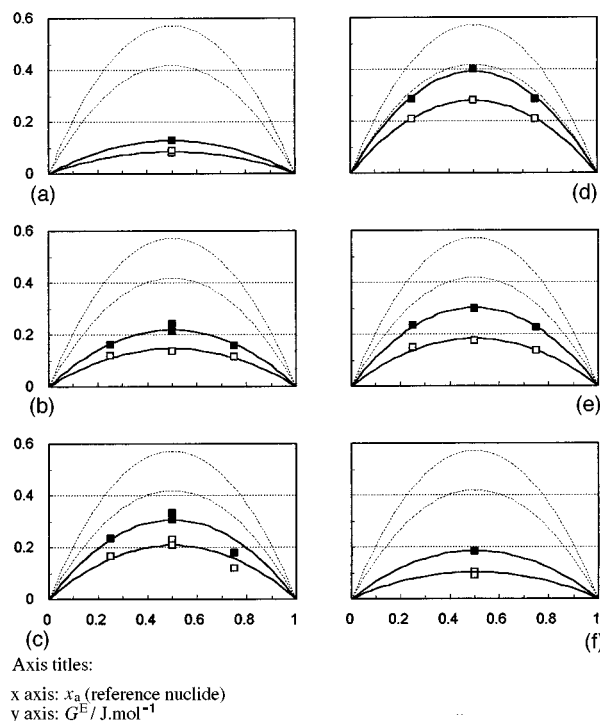


FIG. 1. Plots of  $G^E$  as a function of liquid mole fraction of the reference species at two selected temperatures:  $\square$  100 K and  $\square$  120 K. The heavy lines represent the systems with partially deuterated molecules whereas the light ones represent, for comparison purposes, the corresponding two isotherms for the  $(\text{CH}_4 + \text{CD}_4)$  system (Ref. 1). (a)  $(\text{CH}_4 + \text{CH}_3\text{D})$ ; (b)  $(\text{CH}_4 + \text{CH}_2\text{D}_2)$ ; (c)  $(\text{CH}_4 + \text{CHD}_3)$ ; (d)  $(\text{CH}_3\text{D} + \text{CD}_4)$ ; (e)  $(\text{CH}_2\text{D}_2 + \text{CD}_4)$ ; (f)  $(\text{CHD}_3 + \text{CD}_4)$ .

on triple-point data assumes the existence of structural similarities between the high-temperature solid and liquid phases, and is only valid for temperatures near the triple-point temperature. However, if the density shift at the triple point is well characterized, the Grüneisen parameters can be estimated from fitted sets of frequency data (each set corresponding to the solid and liquid phases near the triple point).

In Table III the calculated spectroscopic data<sup>7</sup> and the Grüneisen parameters necessary to calculate the excess molar Gibbs energy [Eq. (3)] are given. Two methods for obtaining the Grüneisen parameters were employed. In method I, the Grüneisen parameters found for the  $(\text{CH}_4 + \text{CD}_4)$  system<sup>1</sup> were used; these values were calculated assuming the following approximations: (i) The  $\Gamma$  parameters are the same for all isotopic species; (ii) for the internal degrees of freedom only stretching modes are considered (have nonzero  $\Gamma$ ) and the calculations are performed just for the completely symmetrical stretching mode; (iii) for the external degrees of freedom only translational modes are considered. In method II none of the above approximations is taken into account, the Grüneisen parameters being calculated for each mode from the total set of frequencies reported by Bigeleisen *et al.*<sup>7</sup> Frequencies labeled by these authors as “solid” were assumed to represent the real set of frequencies in the solid as well as those reported as “liquid” were taken for the liquid. Combination of the shifts in frequency with the den-

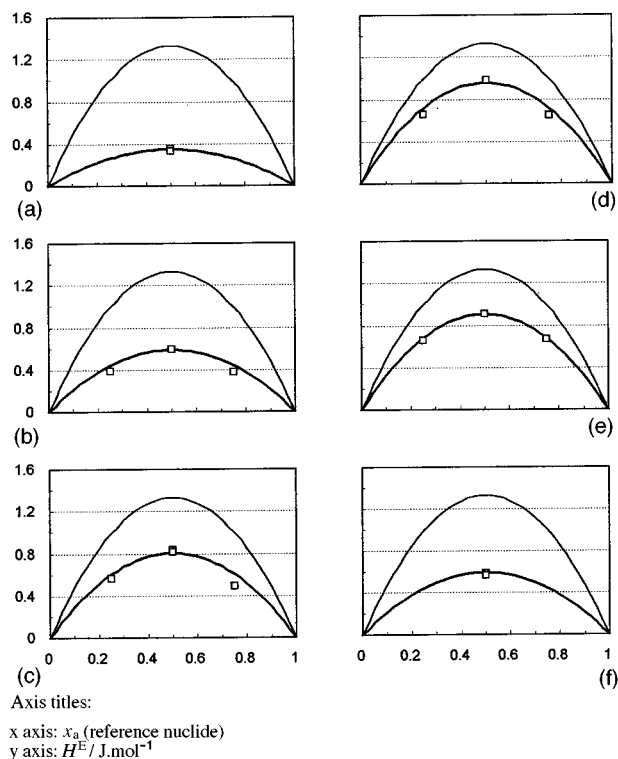


FIG. 2. Plots of  $H^E$  as a function of liquid mole fraction of the reference species. The heavy lines represent the systems with partially deuterated molecules, whereas the light ones represent, for comparison purposes, the corresponding result for the  $(\text{CH}_4 + \text{CD}_4)$  system (Ref. 1). (a)  $(\text{CH}_4 + \text{CH}_3\text{D})$ ; (b)  $(\text{CH}_4 + \text{CH}_2\text{D}_2)$ ; (c)  $(\text{CH}_4 + \text{CHD}_3)$ ; (d)  $(\text{CH}_3\text{D} + \text{CD}_4)$ ; (e)  $(\text{CH}_2\text{D}_2 + \text{CD}_4)$ ; (f)  $(\text{CHD}_3 + \text{CD}_4)$ .

sity difference occurring at the triple-point originates the Grüneisen parameters reported in Table III.

The calculated excess molar Gibbs energy values are given in Table IV. For comparative purposes, experimental values are also included. Both methods originate very similar estimated values which, in turn, agree favorably with the experimental ones. However, a careful analysis of the experi-

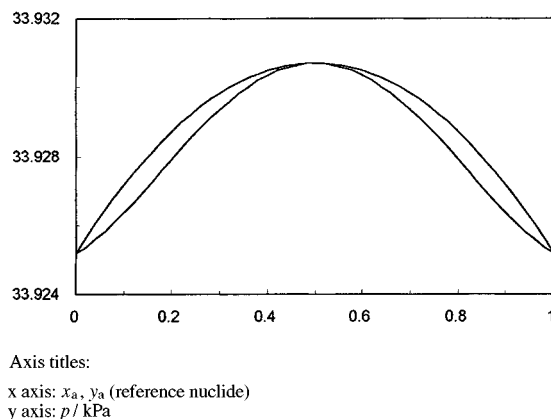


FIG. 3. Modified  $p$ - $x$ - $y$  diagram for the  $(\text{CH}_4 + \text{CH}_3\text{D})$  system at its cross-over temperature. The shown diagram emphasizes the existence of an azeotrope at this particular temperature by enlarging by a factor of  $10^3$  the difference between the vapor and liquid boundary lines.

TABLE III. Calculated spectroscopical data (Ref. 7),  $\bar{\nu}$ , and estimated Grüneisen parameters,  $\gamma$ , necessary to the calculation of  $G^E$  through Eq. (3). The given Grüneisen parameters are those calculated by method II (see the text). In the case of method I (see Ref. 1), all  $\gamma$  values are considered the same for all species and are null except for all the stretching modes ( $\gamma = -0.00311$ ) and all translational modes ( $\gamma = 1.79$ ).

Mode type	CH <sub>4</sub>		CH <sub>3</sub> D		CH <sub>2</sub> D <sub>2</sub>		CHD <sub>3</sub>		CD <sub>4</sub>	
	$\bar{\nu}/\text{cm}^{-1}$	$\gamma$	$\bar{\nu}/\text{cm}^{-1}$	$\gamma$	$\bar{\nu}/\text{cm}^{-1}$	$\gamma$	$\bar{\nu}/\text{cm}^{-1}$	$\gamma$	$\bar{\nu}/\text{cm}^{-1}$	$\gamma$
Stretching	3140	-7.5	3140	-7.4	3139	-7.2	3137	-7.4	2322	-5.0
	3140	-7.5	3140	-7.4	3136	-7.8	2322	-5.1	2322	-5.0
	3140	-7.5	3134	-7.8	2322	-5.3	2322	-5.1	2322	-5.0
	3132	-8.3	2269	-6.6	2269	-6.7	2243	-7.4	2216	-5.8
Bending	1570	12.0	1509	12.8	1473	13.3	1324	12.9	1111	12.0
	1570	12.0	1509	12.8	1360	11.9	1324	12.9	1111	12.0
	1353	17.4	1348	15.5	1274	14.9	1060	14.0	1024	14.1
	1353	17.4	1194	16.2	1123	17.0	1060	14.0	1024	14.1
	1353	17.4	1194	16.2	1058	14.8	1032	16.7	1024	14.1
Translation	77.7	1.2	77.1	1.2	76.3	1.1	72.4	1.2	69.5	1.2
	77.7	1.2	77.1	1.2	74.5	1.2	72.4	1.2	69.5	1.2
	77.7	1.2	75.4	1.2	73.2	1.2	71.3	1.2	69.5	1.2
Rotation	72.3	-0.6	72.3	-0.6	62.7	-0.5	56.2	-0.6	51.1	-0.6
	72.3	-0.6	60.7	-0.6	59.0	-0.6	56.2	-0.6	51.1	-0.6
	72.3	-0.6	60.7	-0.6	54.1	-0.6	51.1	-0.6	51.1	-0.6

mentally determined nonideality of these mixtures shows that  $G^E$  is not a linear function of the number of isotopically substituted hydrogens. In other words, one should expect that the following simple relations (arithmetic mean rules) would be observed for a given temperature and mixture composition:

$$\begin{aligned} G^E(\text{CH}_2\text{D}_2 + \text{CH}_4) &= G^E(\text{CH}_2\text{D}_2 + \text{CD}_4) \\ &= 1/2 G^E(\text{CH}_4 + \text{CD}_4), \end{aligned} \quad (4a)$$

$$\begin{aligned} G^E(\text{CH}_3\text{D} + \text{CH}_4) &= G^E(\text{CHD}_3 + \text{CD}_4) \\ &= 1/4 G^E(\text{CH}_4 + \text{CD}_4), \end{aligned} \quad (4b)$$

$$\begin{aligned} G^E(\text{CHD}_3 + \text{CH}_4) &= G^E(\text{CH}_3\text{D} + \text{CD}_4) \\ &= 3/4 G^E(\text{CH}_4 + \text{CD}_4). \end{aligned} \quad (4c)$$

This was not experimentally observed; instead, one finds that the binary mixtures with CH<sub>4</sub> are clearly more ideal than those with CD<sub>4</sub>. Even though both methods (I and II) give good quantitative agreement with experiment for each individual binary mixture, only method II is able to predict and explain why a deviation from the arithmetic mean rule occurs. Method I estimates that mixtures containing CH<sub>4</sub> are slightly less ideal than the corresponding ones with CD<sub>4</sub>, because both the external and internal frequencies of vibration increase with the decrease of deuterium content and the Grüneisen parameters were held constant upon isotopic substitution [see Eq. (3)]. In method II the Grüneisen parameters are estimated for each isotopic species and for each normal mode of vibration. The external Grüneisen parameters (Table III) do not change upon isotopic substitution but the internal ones do. Therefore, while the external contribution to  $G^E$  [second term in Eq. (3)] follows an arithmetic mean rule, the internal contribution [first term in Eq. (3)] does not, and consequently the total  $G^E$  value also deviates from such rule. The internal contribution to  $G^E$  is, in turn, the sum of two terms of opposite signs corresponding to stretchings (with

negative  $\Gamma\Gamma$ ) and bendings (with positive  $\Gamma\Gamma$ ), which show a trend as we go on an isotopic replacement series from CH<sub>4</sub> to CD<sub>4</sub>: The relative contribution of the bending modes increases with respect to that of the stretching modes and, this way, the internal contribution increases as well as one moves from CH<sub>4</sub> to CD<sub>4</sub>. Consequently, systems containing CD<sub>4</sub> exhibit larger  $G^E$  and  $H^E$  values than the analogous ones with CH<sub>4</sub>.

## B. Comparison with LVIFF measurements

Liquid-vapor isotope fractionation factors (LVIFF),  $\alpha = (xy'/x'y)$ , are related to VPIE,  $(p'/p)$ . In a previous paper<sup>10</sup> we derived an almost exact equation for these two quantities, for a binary system

TABLE IV. Theoretical and experimental  $G^E$  and  $H^E$  values for the equimolar composition at two different temperatures. The subscripts int. and ext. represent the contributions of the internal and external modes of vibration to the theoretical  $G^E$  value. The subscripts th. and expt. stand for the theoretical and experimental values.

System	<i>T</i> /K	$G_{\text{int.}}^E$ (J/mol)	$G_{\text{ext.}}^E$ (J/mol)	$G_{\text{th.}}^E$ (J/mol)	$G_{\text{expt.}}^E$ (J/mol)	$H_{\text{th.}}^E$ (J/mol)	$H_{\text{expt.}}^E$ (J/mol)
CH <sub>4</sub> +CD <sub>4</sub>	100	0.27	0.49	0.76	0.60	1.81	1.54
	120	0.22	0.33	0.56	0.43		
CH <sub>4</sub> +CH <sub>3</sub> D	100	0.05	0.06	0.11	0.13	0.26	0.34
	120	0.04	0.04	0.08	0.09		
CH <sub>4</sub> +CH <sub>2</sub> D <sub>2</sub>	100	0.11	0.13	0.23	0.22	0.54	0.59
	120	0.09	0.09	0.17	0.15		
CH <sub>4</sub> +CHD <sub>3</sub>	100	0.17	0.19	0.36	0.31	0.84	0.80
	120	0.14	0.13	0.27	0.21		
CH <sub>3</sub> D+CD <sub>4</sub>	100	0.21	0.20	0.41	0.39	0.92	0.95
	120	0.17	0.13	0.30	0.28		
CH <sub>2</sub> D <sub>2</sub> +CD <sub>4</sub>	100	0.15	0.13	0.28	0.30	0.63	0.90
	120	0.12	0.09	0.21	0.18		
CHD <sub>3</sub> +CD <sub>4</sub>	100	0.08	0.07	0.15	0.18	0.33	0.59
	120	0.06	0.04	0.11	0.10		

$$\ln \alpha + \ln \left( \frac{\gamma}{\gamma'} \right) = \ln \left( \frac{p'}{p} \right) \left\{ 1 + \frac{p}{RT} \left[ B' - x' \Delta B - V' + x' \Delta V + \frac{1}{2RT} (C' - B'^2)(p + p') + \frac{1}{2} \beta_T V(p + p') \right] \right\} + \frac{(\Delta V - \Delta B)}{RT} p^E + \frac{p_m \delta}{RT} (y' - y), \quad (5)$$

where the prime indicates the lighter isotope,  $\alpha$  is the liquid–vapor isotope fractionation factor,  $\gamma$ , the activity coefficient in the liquid phase,  $x$  and  $y$  the mole fractions in the liquid and gas phases, respectively,  $p$  and  $p_m$  the vapor pressure of each pure component and of the mixture, respectively,  $B$  and  $C$  the second and third virial coefficients (volume expansion),  $V$  the molar volume,  $\beta_T$  the isothermal compressibility coefficient and  $\delta$  the deviation of the cross second virial coefficient,  $B_{12}$ , from the arithmetic mean-rule value:  $\delta = 2B_{12} - B - B'$ . In deriving Eq. (5) we assumed a null isotope effect for the third virial coefficient as well as for the isothermal compressibility. Also the excess molar volume of the liquid phase was taken as zero.

For comparison with the available values of  $\alpha$  at infinite dilution of CD<sub>3</sub>H in CH<sub>4</sub>,  $\alpha^\infty$ , Eq. (5) can be transformed accordingly, by putting  $x' = 1$ ,  $\gamma' = 1$ , and  $p^E = 0$

$$\ln \alpha^\infty + \ln \gamma^\infty = \ln \left( \frac{p'}{p} \right) \left\{ 1 + \frac{p}{RT} \left[ B - V + \frac{1}{2RT} (C' - B'^2)(p + p') + \frac{1}{2} \beta_T V(p + p') \right] \right\} + \frac{p_m \delta}{RT} (y' - y). \quad (6)$$

Within the framework of the Bigeleisen's theory of isotope effects<sup>4,10,15</sup> it can be shown that the so-called ratio (condensed over gas phase) of reduced partition functions ratio (RPFR),  $f_c/f_g$  is approximately given by

$$\ln \left( \frac{f_c}{f_g} \right) = \ln \left( \frac{p'}{p} \right) \left\{ 1 + \frac{p}{RT} \left[ B - V + \frac{1}{2RT} (C' - B'^2) \times (p + p') + \frac{1}{2} \beta_T V(p + p') \right] \right\}. \quad (7)$$

Combining Eqs. (6) and (7),

$$\ln \alpha^\infty + \ln \gamma^\infty = \ln \left( \frac{f_c}{f_g} \right) + \frac{p_m \delta}{RT} (y' - y). \quad (8)$$

Since the second term in Eq. (8)—related to the excess energy of mixing for the gas phase—is expected to be very

small in comparison with the other term, values of  $\ln \gamma^\infty$  (and consequently values for  $G^E$  of the liquid phase) can be inferred from this equation. Were values of  $\alpha^\infty$  sufficiently accurate and one could make quantitative estimates of  $\gamma$  values from the difference between LVIFF and VPIE, although these last two quantities are much larger than the former.

Popowicz *et al.*<sup>11</sup> compared his LVIFF results with VPIE data taken from Armstrong *et al.*<sup>6</sup> and concluded that the least-squares fitted *absolute* values of the experimental  $\alpha$  were three percent larger than the corresponding ones derived from VPIE data,  $\ln(f_c/f_g)$ . In other words,  $\ln \gamma^\infty = -0.03 \ln \alpha^\infty$ . In the temperature range 100–120 K, this corresponds to values of  $\ln \gamma^\infty$  between  $3 \times 10^{-4}$  and  $6 \times 10^{-4}$ , to be compared with our experimental values between of  $8 \times 10^{-4}$  and  $15 \times 10^{-4}$  (see Table II,  $\ln \gamma^\infty = A + B/T$ ). Considering that the scatter of LVIFF data is much larger than the obtained value for  $\ln \gamma$ , the relatively good agreement is somewhat fortuitous. As a matter of fact, if our set of VPIE results<sup>10</sup> is used instead of that of Armstrong *et al.*<sup>6</sup> the agreement is lost, although the difference between the two sets of VPIE data is still very small.

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