ISOTHERMAL AND ISOBARIC VAPOUR-LIQUID EQUILIBRIUM DATA IN THE TETRACHLOROMETHANE-n-BUTYL ALCOHOL SYSTEM*

Jan LINEK

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6 - Suchdol

Received November 17th, 1982

Isothermal vapour-liquid equilibrium data at 65, 73 and 80°C and isobaric ones at 101·3 kPa were measured in the tetrachloromethane-n-butyl alcohol system. A modified circulation still of the Gillespie type was used for the measurements. Under the conditions of measurements, the system exhibits positive deviations from Raoult's law and minimum boiling-point azeotropes. The experimental data were fitted to a number of correlation equations. The best correlation was reached with the Wilson equation but the regression failed in some cases. Therefore the results for the 5th order Redlich-Kister equation are presented.

As continuation of our previous studies[1-3] of vapour-liquid equilibria in the tetrachloromethane-isobutyl alcohol, -tert-butyl alcohol and -sec-butyl alcohol systems, the equilibrium data in the tetrachloromethane-n-butyl alcohol system have been measured isothermally at three temperatures and isobarically at normal atmospheric pressure.

EXPERIMENTAL

Substances used. Tetrachloromethane, analytical reagent grade (Lachema, Brno, Czechoslovakia), was twice rectified on a fifty-plate bubble-cup column. n-Butyl alcohol, analytical reagent grade (Lachema, Brno, Czechoslovakia), was dried with anhydrous potassium carbonate, and distilled from sodium twice on a fifty-plate bubble-cup column[4]. No impurities in the n-butyl alcohol used were detected by gas chromatographic analysis. The water content was less than 0·02%. The measured values of physical constants (density, refractive index and normal boiling point) and their comparison with the literature values are given in Table I along with the used values of constants of the Antoine vapour pressure equation

$$\log P^s = A - B/(t + C)\,, \qquad (1)$$

where P^s is in kPa and t in °C.

The constants A, B, C for tetrachloromethane were taken from the literature[7] whereas those for n-butyl alcohol were established from our vapour pressure data.

---

* Part XCVII in the series Liquid-Vapour Equilibrium; Part XCVI: This Journal *48*, 2446 (1983).

Saturated vapour pressure measurement. Saturated vapour pressures for n-butyl alcohol were measured by means of the standard Swietoslawski ebulliometer connected, in parallel with the second ebulliometer filled with redistilled water, to a buffer reservoir of the pressure-controlling assembly. Further details of the measurement are given below. The experimental data along with the data calculated from the evaluated[8] values of the Antoine equation (*1*) are given in Table II.

Analytical method. The samples of the equilibrium vapour and liquid phases were analyzed refractometrically at 20°C. To this purpose, an Abbe-type refractometer (Carl Zeiss, Jena) was used allowing to measure refractive indices with an accuracy of ±0·0001. Using a set of calibration binary mixtures, constants of the relation

$$n_D = x_1 n_{D1} + x_2 n_{D2} + x_1 x_2 (x_1 A_1 + x_2 Aa - x_1 x_2 A_3) \qquad (2)$$

were computed. Here x_1 is the mole fraction of tetrachloromethane, $x_2 = 1 - x_1$, n_D is the refractive index of mixture, n_{D1}, n_{D2} those of pure components and A_1, A_2, A_3 are the constants evaluated from the measured (at 20°C) calibration samples by the least-squares method ($A_1 = -0{\cdot}00304$, $A_2 = 0{\cdot}00856$, $A_3 = -0{\cdot}01237$). Eq. (*2*) with the constants represents the experimental points with an average absolute deviation in n_D 0·00004 and a mean per cent deviation 0·07%. Calibration interpolation tables were computed for direct reading the sample composition from measured n_D values.

Apparatus and procedure. The measurements of vapour-liquid equilibrium were carried out in a modified Gillespie still. The description of the apparatus and measuring procedure can be found in the literature[9]. The pressure in the system was established by measuring boiling point of redistilled water in an ebulliometer connected in parallel to the equilibrium still. Temperature was measured by mercury-in-glass calorimetric standards calibrated by means of a Mueller

TABLE I

Physical properties of pure substances and Antoine vapour pressure constant

Property	Tetrachloromethane			n-Butyl alcohol		
	measured	literature	ref.	measured	literature	ref.
Density, d_4^{20}	1·5939	1·5939 — 1·59404	5, 6	0·80962	0·80961—0·8097	5, 6
Refractive index n_D^{20}	1·4601	1·46005—1·46036	5, 6	1·3992	1·3992 — 1·3993	5, 6
Boiling point, °C	76·83	76·65—76·76	5, 6	117·59	117·6—117·8	5, 6
Antoine vapour pressure constants						
A		6·00416			6·52572	
B		1 212·021			1 326·735	
C		226·409			175·937	

bridge with platinum resistance thermometer (Leeds and Northrup). The equilibrium samples were taken for analysis only if the boiling point in the still was not changing for 30 minutes.

RESULTS AND DISCUSSION

The experimental vapour–liquid equilibrium data for the isothermal conditions of 65, 73 and 80°C are given in Tables III, IV and V, respectively. The values for the isobaric condition of 101·3 kPa are presented in Table VI.

The equation of vapour–liquid equilibrium in a binary system can be written in the form

$$y_iP = \gamma_i x_i P_i^s \exp\left\{\left[(B_{ii} - V_i)(P_i^s - P) - P\left(2\sum_{j=1}^{2} y_jB_{ij} - B_{ii} - B\right)\right]/RT\right\} \qquad (3)$$

TABLE II

Saturated vapour pressures of n-butyl alcohol

	t, °C	P_{exp}, kPa	Dev[a], kPa	Per cent
	67·695	12·055	−0·031	−0·25
	76·730	18·846	−0·018	−0·10
	80·300	22·303	−0·022	−0·10
	83·980	26·320	0·059	0·22
	89·040	33·007	0·009	0·03
	90·400	34·950	0·069	0·20
	93·020	39·158	0·000	0·00
	96·720	45·668	0·016	0·04
	98·830	49·857	−0·068	−0·14
	100·310	52·790	0·054	0·10
	102·310	57·224	−0·007	−0·01
	104·460	62·229	0·012	0·02
	106·210	66·646	−0·053	−0·08
	109·285	74·934	−0·095	−0·13
	110·750	79·109	−0·061	−0·08
	112·380	83·970	−0·013	−0·02
	113·905	88·801	−0·030	−0·03
	115·740	94·849	0·008	0·01
	116·685	98·078	0·042	0·04
	117·240	99·958	0·120	0·12
Standard deviation			0·055	

[a] Dev = $P_{exp} - P_{calc}$; Antoine vapour pressure constants: $A = 6·52572$, $B = 1\ 326·735$, $C = 175.937$.

which is derived for the standard state of pure component at temperature T and pressure P of the system, assuming pressure independent pure component liquid molar volumes V_i and the validity of the volume explicit virial expansion truncated after the second term for the vapour phase. In Eq. (*3*), γ_i is the activity coefficient, x_i and y_i are the mole fractions of the liquid and vapour phase, respectively, B_{ii} and P_i^s are the second virial coefficient and saturated vapour pressure of pure i-th

TABLE III

Isothermal vapour-liquid equilibrium data in the tetrachloromethane(1)-n-butyl alcohol(2) system at 65°C and their comparison with calculated values

Experimental			Calculated deviations[a]			
x	y	P, kPa	Δx	Δy	ΔP, kPa	ΔT, K
0·0130	0·1741	12·93	−0·0025	0·0002	0·46	0·00
0·0580	0·4895	20·35	−0·0038	0·0007	1·12	0·00
0·1006	0·6385	26·71	−0·0043	0·0015	0·88	0·00
0·1770	0·7626	36·48	−0·0020	0·0017	0·25	0·00
0·2390	0·8084	42·91	0·0007	−0·0012	−0·03	0·00
0·2970	0·8396	47·98	−0·0002	0·0006	−0·18	0·00
0·3420	0·8551	51·38	−0·0001	0·0005	0·00	0·00
0·4065	0·8774	55·08	−0·0012	0·0056	−0·15	0·00
0·4470	0·8825	57·13	−0·0004	0·0023	−0·09	0·00
0·4672	0·8875	58·11	−0·0006	0·0033	−0·06	0·00
0·5085	0·8943	57·90	−0·0001	0·0027	−2·04	0·00
0·5330	0·8976	61·01	−0·0003	0·0019	0·06	0·00
0·6100	0·9076	63·47	0·0000	0·0001	−0·27	0·00
0·6632	0·9145	65·15	0·0000	−0·0002	−0·21	0·00
0·7821	0·9310	67·86	−0·0003	0·0026	−0·08	0·00
0·8154	0·9343	69·00	−0·0003	0·0024	0·56	0·00
0·8345	0·9360	69·06	−0·0002	0·0019	0·37	0·00
0·8875	0·9490	70·11	−0·0014	0·0072	0·72	0·00
0·9293	0·9555	70·65	−0·0012	0·0034	0·75	0·00
0·9603	0·9667	70·86	−0·0007	0·0011	0·68	0·00
0·9906	0·9906	70·65	−0·0008	0·0008	0·52	0·00
Mean absolute			0·0010	0·0020	0·45	0·00
Root mean square			0·0015	0·0027	0·65	0·00
Standard			0·0017	0·0030	0·73	0·00

[a] Constants of the Redlich–Kister 5th order equation: $A_1 = 1{\cdot}2653$, $A_2 = 0{\cdot}4192$, $A_3 = 0{\cdot}1551$, $A_4 = 0{\cdot}3163$; virial coefficients: $B_{11} = -1\,180{\cdot}4$ ml/mol, $B_{22} = -2\,740{\cdot}7$ ml/mol, $B_{12} = -922{\cdot}2$ ml/mol; liquid molar volumes: $V_1 = 102{\cdot}1$ ml/mol, $V_2 = 96{\cdot}6$ ml/mol.

component, respectively, B_{ij} is the second cross virial coefficient and R the gas constant. The second virial coefficients required for calculations were estimated by the

TABLE IV

Isothermal vapour-liquid equilibrium data in the tetrachloromethane(1)-n-butyl alcohol(2) system at 73°C and their comparison with calculated values

Experimental			Calculated deviations[a]			
x	y	P, kPa	Δx	Δy	ΔP, kPa	ΔT, K
0·0043	0·0420	16·14	−0·0001	0·0000	0·19	0·00
0·0116	0·1230	18·84	−0·0020	0·0002	1·15	0·00
0·0260	0·2280	19·72	−0·0011	0·0002	0·11	0·00
0·0376	0·3201	23·45	−0·0034	0·0004	1·27	0·00
0·0976	0·5535	34·98	0·0036	−0·0019	2·96	−0·01
0·1170	0·6260	38·83	−0·0026	0·0005	1·92	0·00
0·1741	0·7290	47·95	−0·0036	0·0026	0·61	0·00
0·2233	0·7803	54·93	−0·0035	0·0044	0·03	0·00
0·2891	0·8206	61·37	−0·0017	0·0048	−1·44	0·01
0·2986	0·8136	62·18	0·0027	−0·0046	−1·19	0·00
0·3356	0·8296	66·32	0·0017	−0·0041	−0·72	0·00
0·3390	0·8330	66·49	0·0011	−0·0022	−0·91	0·00
0·3950	0·8570	71·11	−0·0009	0·0043	−0·80	0·00
0·4340	0·8640	74·04	−0·0003	0·0020	−0·39	0·00
0·4470	0·8706	74·68	−0·0011	0·0056	0·56	0·00
0·5120	0·8842	78·08	−0·0010	0·0065	−0·65	0·00
0·5396	0·8810	79·05	0·0004	−0·0013	−0·94	0·00
0·6065	0·8926	82·47	0·0001	−0·0006	−0·39	0·00
0·6740	0·9026	84·72	0·0001	−0·0004	−0·53	0·00
0·7184	0·9093	86·57	0·0000	0·0003	0·01	0·00
0·7840	0·9176	88·14	0·0000	0·0001	0·02	0·00
0·8415	0·9260	89·37	−0·0001	0·0004	0·16	0·00
0·9010	0·9410	90·68	−0·0009	0·0033	0·47	0·00
0·9360	0·9506	91·21	−0·0005	0·0010	0·52	0·00
0·9635	0·9651	91·41	−0·0004	0·0005	0·53	0·00
0·9921	0·9875	90·88	0·0012	−0·0011	0·23	0·00
Mean absolute			0·0013	0·0020	0·72	0·00
Root mean square			0·0018	0·0028	0·97	0·00
Standard			0·0019	0·0031	1·05	0·00

[a] Constants of the Redlich–Kister 5th order equation: $A_1 = 1{\cdot}2343$, $A_2 = 0{\cdot}4442$, $A_3 = 0{\cdot}0754$, $A_4 = 0{\cdot}3010$; virial coeficients: $B_{11} = -1\,107{\cdot}6$ ml/mol, $B_{22} = -2\,306{\cdot}4$ ml/mol, $B_{12} = -869{\cdot}7$ ml/mol; liquid molar volumes: $V_1 = 103{\cdot}1$ ml/mol, $V_2 = 97{\cdot}5$ ml/mol.

method of Hayden and O'Connell[10], and are given at the bottom of Tables III–V. For isobaric data, the temperature dependence in the form

$$\log(-B_{mn}) = k_1 + k_2/T \tag{4}$$

was used in Table VI, where k_1, k_2 are adjustable parameters, B_{mn} is in ml/mol and T in K. The liquid molar volumes (densities) of pure components were found for several temperatures in the literature[5], and their temperature dependence was calculated from the relation

$$V_i = K_1/(1 - K_2T), \tag{5}$$

where K_1 and K_2 are adjustable parameters and V_i is in ml/mol.

The experimental data were fitted to the following correlation relations[8]: Redlich–Kister equation of the 3rd, 4th and 5th order, van Laar–Null equation, the Wilson equation and the Renon–Prausnitz (NRTL) equation. As a results of computations, the 5th order Redlich–Kister equation

$$\log \gamma_1 = x_2^2[A_1 + A_2(3x_1 - x_2) + A_3(x_1 - x_2)(5x_1 - x_2) + + A_4(x_1 - x_2)^2(7x_1 - x_2)], \tag{6a}$$

$$\log \gamma_2 = x_1^2[A_1 + A_2(x_1 - 3x_2) + A_3(x_1 - x_2)(x_1 - 5x_2) + + A_4(x_1 - x_2)^2(x_1 - 7x_2)], \tag{6b}$$

(A_1, A_2, A_3, A_4 are adjustable constants) was used to represent the composition dependence of liquid-phase activity coefficients in Tables III–VI. Despite only two constants the Wilson equation gives practically the same deviations as Eq. (6) but, unfortunately, the regression failed in some cases.

The parameters of the correlation relations were evaluated using the maximum likelihood method. The minimized objective function has the form

$$S = \sum_{n=1}^{N}\left[\frac{(x_n^e - x_n^t)^2}{\sigma_{x_n}^2} + \frac{(y_n^e - y_n^t)^2}{\sigma_{y_n}^2} + \frac{(T_n^e - T_n^t)^2}{\sigma_{T_n}^2} + \frac{(P_n^e - P_n^t)}{\sigma_{P_n}^2}\right], \tag{7}$$

where n denotes the n-th experimental point, N is the total number of experimental points, σ^2 are estimated variances of respective variables and the superscripts e and t denote the experimental and "true" values, respectively, of the variable corresponding to the given experimental point. The estimated uncertainties in measured quantities are as follows: $\Delta x = \Delta y = 0{\cdot}002$, $\Delta P = 1{\cdot}0$ kPa, $\Delta P = 0{\cdot}03$ K. The simplex method by Nelder and Mead[11] was used to minimize the objective function (7).

As it can be seen from Tables III – VI, the system tetrachloromethane–n-butyl alcohol exhibits positive deviations from ideal behaviour of the liquid phase with a minimum-boiling azeotrope. At normal atmospheric pressure (101·325 kPa), the coordinates of the azeotropic point estimated from our data are 95·6 mol% tetrachloromethane and 76·4°C which is in reasonable agreement with two literature values reported by Hersley[12], *viz.*, 95·0 and 95·1 mol% tetrachloromethane and 76·55°C.

TABLE V

Isothermal vapour–liquid equilibrium data in the tetrachloromethane(1)–n-butyl alcohol(2) system at 80°C and their comparison with calculated values

Experimental			Calculated deviations[a]			
x	y	P, kPa	Δx	Δy	ΔP, kPa	ΔT, K
0·0304	0·3083	31·17	−0·0037	0·0005	0·35	0·00
0·0594	0·4470	37·52	−0·0021	0·0005	−0·07	0·00
0·1036	0·5853	47·62	−0·0033	0·0016	−0·31	0·00
0·1410	0·6471	54·49	0·0004	0·0000	−0·33	0·00
0·2201	0·7273	66·67	0·0051	−0·0053	−1·00	0·00
0·2403	0·7520	71·40	0·0000	0·0000	0·03	0·00
0·2733	0·7786	75·84	−0·0023	0·0042	−0·22	0·00
0·3260	0·8031	82·40	−0·0014	0·0029	0·27	0·00
0·3652	0·8206	87·11	−0·0020	0·0044	0·89	0·00
0·4895	0·8500	97·13	0·0006	−0·0030	0·67	0·00
0·5853	0·8740	102·38	0·0001	−0·0004	−0·17	0·00
0·6615	0·8875	106·08	0·0001	−0·0006	−0·11	0·00
0·7240	0·9010	108·93	−0·0005	0·0032	0·48	0·00
0·7820	0·9093	110·78	−0·0005	0·0032	0·76	0·00
0·8154	0·9130	111·88	−0·0004	0·0019	1·11	0·00
0·8535	0·9175	112·67	0·0000	−0·0002	1·13	0·00
0·8842	0·9260	111·80	−0·0003	0·0013	−0·29	0·00
0·9176	0·9391	112·67	−0·0014	0·0034	0·04	0·00
0·9540	0·9586	113·22	−0·0023	0·0033	0·33	0·00
0·9875	0·9860	112·35	−0·0012	0·0010	0·00	0·00
Mean absolute			0·0014	0·0021	0·43	0·00
Root mean square			0·0020	0·0026	0·56	0·00
Standard			0·0022	0·0029	0·63	0·00

[a] Constants of the Redlich–Kister 5th order equation: $A_1 = 1·2570$, $A_2 = 0·3596$, $A_3 = 0·2323$, $A_4 = 0·1610$; virial coefficients: $B_{11} = -1\,049·8$ ml/mol, $B_{22} = -2\,005·0$ ml/mol, $B_{12} = -827·5$ ml/mol; liquid molar volumes: $V_1 = 104·0$ ml/mol, $V_2 = 98·4$ ml/mol.

TABLE VI

Isobaric vapour–liquid equilibrium data in the tetrachloromethane(1)–n-butyl alcohol(2) system at 101·3 kPa and their comparison with calculated values

Experimental			Calculated deviations[a]			
x	y	T, K	Δx	Δy	ΔT, K	ΔP, kPa
0·0101	0·0653	115·55	−0·0001	−0·0005	0·00	1·28
0·0333	0·1833	112·66	0·0021	−0·0005	0·00	0·02
0·0378	0·2080	111·86	0·0017	−0·0005	0·00	0·30
0·0696	0·3455	107·32	0·0017	−0·0010	0·00	0·95
0·0890	0·4100	103·57	0·0035	−0·0044	−0·02	5·94
0·1140	0·4880	101·90	0·0016	−0·0016	−0·01	1·44
0·1470	0·5655	96·68	0·0028	−0·0068	−0·03	7·64
0·1970	0·6560	94·72	0·0001	0·0003	0·00	−0·47
0·2201	0·6880	93·36	−0·0003	0·0019	0·01	−1·69
0·2230	0·6935	92·53	−0·0011	0·0009	0·00	0·14
0·2530	0·7273	90·60	−0·0012	0·0015	0·00	0·00
0·2765	0·7460	89·40	0·0003	0·0000	0·00	−0·31
0·2940	0·7560	88·80	0·0022	−0·0023	0·00	−1·10
0·3325	0·7910	86·47	−0·0011	0·0024	0·00	−0·10
0·3536	0·7961	86·05	0·0017	−0·0024	0·00	−1·24
0·3850	0·8190	85·76	−0·0002	0·0058	0·02	−4·40
0·4165	0·8330	83·56	−0·0008	0·0032	0·00	−0·64
0·4200	0·8330	83·77	−0·0003	0·0028	0·01	−1·60
0·4501	0·8415	82·54	0·0001	−0·0002	0·00	−0·29
0·4775	0·8450	82·06	0·0013	−0·0045	0·00	−0·80
0·4826	0·8535	81·59	−0·0004	0·0014	0·00	0·23
0·5206	0·8640	80·91	−0·0005	0·0023	0·00	−0·01
0·5415	0·8620	80·75	0·0008	−0·0037	0·00	−0·59
0·5818	0·8756	79·75	−0·0003	0·0010	0·00	0·66
0·6120	0·8740	79·42	0·0007	−0·0055	0·00	0·55
0·6206	0·8756	79·26	0·0007	−0·0054	−0·01	0·75
0·6756	0·8840	78·46	0·0005	−0·0057	−0·01	1·55
0·7113	0·8926	78·19	0·0002	−0·0022	−0·01	1·43
0·7150	0·8955	77·91	−0·0001	−0·0002	−0·01	2·22
0·7770	0·9010	77·30	0·0005	−0·0044	−0·01	2·62
0·7856	0·9010	77·47	0·0007	−0·0055	−0·01	1·89
0·8310	0·9120	76·89	0·0006	−0·0039	−0·01	2·61
0·8470	0·9260	76·92	−0·0017	0·0059	−0·01	2·08
0·8706	0·9260	76·71	−0·0001	−0·0003	−0·01	2·19
0·8976	0·9425	76·48	−0·0025	0·0062	−0·01	2·21
0·9043	0·9425	76·52	−0·0017	0·0039	0·00	1·95
0·9210	0·9490	76·39	−0·0016	0·0031	−0·01	1·98
0·9343	0·9506	76·42	0·0003	−0·0008	−0·01	1·64
0·9683	0·9666	76·37	0·0028	−0·0040	0·00	1·26

TABLE VI
(*Continued*)

	Calculated deviations[a]			
	Δx	Δy	ΔT, K	ΔP, kPa
Mean absolute	0·0010	0·0028	0·01	1·51
Root mean square	0·0014	0·0034	0·01	2·16
Standard	0·0014	0·0036	0·01	2·28

[a] Constants of the Redlich–Kister 5th order equation: $A_1 = 1{\cdot}2139$, $A_2 = 0{\cdot}4168$, $A_3 = 0{\cdot}0779$, $A_4 = -0{\cdot}0104$; temperature dependence of virial coefficients: $\log(-B_{11}) = 1{\cdot}8490 + 413{\cdot}97/T$, $\log(-B_{22}) = 0{\cdot}53315 + 977{\cdot}67/T$, $\log(-B_{12}) = 1{\cdot}8155 + 389{\cdot}33/T$; temperature dependence of liquid molar volumes: $V_1 = 70{\cdot}601/(1 - 9{\cdot}1292 \,.\, 10^{-4}T)$, $V_2 = 71{\cdot}942/(1 - 7{\cdot}3065 \,.\, 10^{-4}T)$.

REFERENCES

1. Linek J., Klimánková J.: This Journal *44*, 3509 (1979).
2. Linek J., Bernatová S.: This Journal *48*, 1669 (1983).
3. Linek J.: This Journal *48*, 2446 (1983).
4. Perrin D. D., Armarego W. L. F., Perrin D. R.: *Purification of Laboratory Chemicals*. Pergamon Press, London 1966.
5. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Elsevier, Amsterdam, Vol. 1, 1950; Vol. 2, 1965.
6. Riddick J. A., Bunger W. B.: in the book: *Techniques of Chemistry* (*Organic Solvents*), Vol. **II** (A. Weisberger, Ed.). Wiley, New York 1970.
7. Boublík T., Fried V., Hála E.: *The Vapour Pressures of Pure Substances*. Elsevier, Amsterdam 1973.
8. Hála E., Aim K., Boublík T., Linek J., Wichterle I.: *Rovnováha kapalina–pára za normálních a nízkých tlaků*. Academia, Prague 1982.
9. Hála E., Pick J., Fried V., Vilím O.: *Vapour–Liquid Equilibrium*, 2nd. Ed. Pergamon Press, London 1967.
10. Hayden J. G., O'Connell J. P.: Ind. Eng. Chem., Process Des. Develop. *14*, 209 (1975).
11. Nelder J. A., Mead R.: Comput. J. *7*, 308 (1964).
12. Horlsey L. H.: *Azeotropic Data* III. Adv. Chem. Ser. 116, Am. Chem. Soc., Washington 1973.

Translated by the author.