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# VAPOUR PRESSURE ISOTOPE EFFECT OF THE EQUIMOLAR H<sub>2</sub>0-D<sub>2</sub>0 MIXTURE

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#### ABSTRACT

Vapour pressure isotope effect (VPIE) of the equimolar  ${\rm H_2O-D_2O}$  mixture in the temperature range 5 to 90  $^{\rm O}{\rm C}$  was measured to investigate the ideality of the  ${\rm H_2O-HDO-D_2O}$  system. A fit of the data resulted in the equation:

$$\ln\left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{mixture}}}\right) = 0.076624 - \frac{88.161}{T} + \frac{25972}{T^2}$$

$$278 < T < 363$$

For comparison the VPIE of the pure H2O-D2O system was redetermined on the same apparatus, here the data can be expressed by the equation:

$$\ln\left(\frac{p_{H_2O}}{p_{D_2O}}\right) = 0.14716 - \frac{173.28}{T} + \frac{51545}{T^2}$$

$$278 < T < 363$$

#### **АННОТАЦИЯ**

С целью выяснения степени идеальности системы H<sub>2</sub>O-HDO-D<sub>2</sub>O нами был измерен изотопный эффект давления пара эквимолекулярной смеси H<sub>2</sub>O-D<sub>2</sub>O в диапазоне температур 5-90°C. Обработка данных по методу наименьших квадратов привела к следующему экспериментальному уравнению:

$$\ln\left(\frac{p_{\text{H}_2\text{O}}}{p_{\text{CMECH}}}\right) = 0.076624 - \frac{88.161}{T} + \frac{25972}{T^2}$$
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Для сравнения в той же установке был определен изотопный эффект давления пара чистой системы  ${\rm H_2O-D_2O}$ , и в результате для логарифма отношений давлений паров  ${\rm H_2O}$  и  ${\rm D_2O}$  было получено следующее уравнение:

$$\ln \left( \frac{p_{H_2O}}{p_{D_2O}} \right) = 0.14716 - \frac{173.28}{T} + \frac{51545}{T^2}$$

$$278 < T < 363$$

#### KIVONAT

Megmértük az ekvimoláris  $\rm H_2O-D_2O$  elegy gőznyomás izotópeffektusát  $\rm 5^{O}$ -tól  $\rm 90^{O}C$ -ig annak vizsgálatára, hogy a  $\rm H_2O-HDO-D_2O$  rendszer ideális-e. Az adatok fittelése az alábbi egyenletet eredményezte:

$$\ln\left(\frac{P_{H_2O}}{P_{elegy}}\right) = 0.076624 - \frac{88.161}{T} + \frac{25972}{T^2}$$
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összehasonlitás céljából a tiszta H<sub>2</sub>O-D<sub>2</sub>O rendszer gőznyomás izotópeffektusát is ujra meghatároztuk ugyanazon a készüléken; itt a következő egyenletet nyertük:

$$\ln \left( \frac{p_{\text{H}_2O}}{p_{\text{elegy}}} \right) = 0.14716 - \frac{173.28}{T} + \frac{51545}{T^2}$$

$$278 < T < 363$$

## 1. INTRODUCTION

During the last decade the precision of vapour pressure isotope effect (VPIE) measurements has significantly improved, due mainly to the development of high sensitivity capacitance-type electronic differential manometers. Using this type of manometer (Datametrics Inc., Mass., USA), in a cooperative work with the Chemistry Department of The University of Tennessee, USA, we recently succeeded in determining the very small VPIE deviation (0.02-0.03 rel.%) from Raoult's law value of equimolar  $C_6H_6-C_6D_6$  and  $C_6H_{12}-C_6D_{12}$  mixtures [1].

The theoretical interpretation of the excess VPIE of these isotopic mixtures shows that this kind of data is very useful with regard to new information on intermolecular interaction and molecular movements in the liquid phase [2].

Due to its great importance and its characteristic structure, the ideal behaviour of water isotopic mixtures has been the subject of research for many years. A recent summation of the earlier measurements is given in the paper of Phutela and Fenby [3]. These investigations, based on vapour pressure [4-6] or boiling point elevation [7] measurements, uniformly showed that there exists a small negative vapour pressure deviation from Raoult's law value in the H2O-HDO-D2O liquid mixture and vapour phase equilibrium, i.e. the vapour pressure of the mixture is higher if it is considered as a two component system instead of a three component system. However, it has been possible to derive the absolute value of this deviation only with a relatively large uncertainty, partly because the error in the VPIE determinations was too large [6], partly because the measurements were not systematic, i.e. the VPIE of the H2O-D2O mixture and that of the pure D2O were not measured by the same laboratory [4,5].

With improved VPIE apparatus and having now carried out the measurements both on the equimolal  ${\rm H_2O-D_2O}$  mixture and on the

pure D<sub>2</sub>O with the use of the same manometer and thermometer we repeated the determination of the excess VPIE in a wide range of temperatures.

### 2. EXPERIMENTAL

<u>Materials:</u> The  $\mathrm{H_2}^{16}\mathrm{O}$  used in the measurements was triply distilled tapwater. A complete isotope analysis of our  $\mathrm{D_2}^{16}\mathrm{O}$  sample was made by Dr. D. Staschewski at the Karlsruhe Nuclear Research Center and given as 99.815 at % D, 0.217 at %  $^{18}\mathrm{O}$  and 0.041 at %  $^{17}\mathrm{O}$ . The D-concentration of the equimolar  $\mathrm{H_2O-D_2O}$  mixture, made up gravimetrically on a Sartorius balance, was found to be 49.936 at %.

Differential vapour pressure apparatus: Values of the isotopic vapour pressure differences and that of the total (absolute) pressure of the normal water sample were measured to four significant figures using an apparatus whose principle is shown in Fig.~1. The samples (2-3 g) were contained in a copper block (A) suspended in a thermostat (B) controlled to  $\pm 0.02$  °C at a temperature between 5 and 90 °C.

The large copper block (80 mm diameter) serves to even out the temperature differences between the sample chambers. Using stainless steel connecting lines and "all-welded" valves, two capacitive pressure transducers (C,D) are joined to the sample chambers. To avoid any parasitic condensation the transducers and the manifold were thermostated around 100  $^{\circ}$ C. It is very important to keep the transducers at a relatively constant temperature ( $\pm 0.1$   $^{\circ}$ C) because their zero and also their calibration are highly sensitive to temperature variation. In view of this, we placed them in a double-walled metal box through which oil was circulated from a thermostat. The temperature of the copper block containing the samples was measured with a platinum resistance thermometer (E) to  $\pm 0.03$   $^{\circ}$ C.

In the first run transducer C measures the pressure difference between the  $\rm H_2O$  and  $\rm D_2O$  samples, while on transducer D - whose reference side is connected to the vacuum line - we measure the total pressure of  $\rm H_2O$ . In the second run the  $\rm D_2O$  sample was

changed to the equimolar  ${\rm H_2O-D_2O}$  mixture. A background measurement (using  ${\rm H_2O}$  samples in both sides of the system) indicates a pressure difference of less than 0.26664 Pa (2×10<sup>-3</sup> mmHg) up to 80  $^{\rm O}$ C. This shows that the temperature difference between the samples is of the order of 0.0001  $^{\rm O}$ C.

Calibration: The pressure transducers were calibrated using a U-type mercury manometer with an inner diameter of 22 mm. Mercury level differences on the manometer were measured with a Russian-made K-2 type cathetometer whose sensitivity was 0.3 Pa (0.002 mmHg). A checking of the calibration was carried out by measuring the triple-point vapour pressure of H<sub>2</sub>O, we agreed with the literature value of 611.66 Pa [8] within the experimental precision (0.2-0.3 rel.%).

The platinum resistance thermometer was calibrated indirectly: we read the absolute vapour pressure of  $\rm H_2O$  on pressure transducer D and calculated the temperature from the vapour pressure equation of  $\rm H_2O$  given by Goff [9]. Here the precision of the pressure readings (0.2-0.3 rel.%) gives an uncertainty of 0.03  $^{\rm O}$ C for the calculated temperature.

Cleaning the apparatus: The vapour pressure apparatus is connected to a high vacuum system containing an oil-diffusion pump. After a couple of measurements we always found a minute quantity of adsorbed diffusion pump oil in the apparatus due to backstreaming from the pump. This occurred in spite of the fact that we used a trap between the apparatus and the vacuum system and this trap was always cooled to dry-ice temperature. Because the oil-contaminant is highly disturbing to VPIE measurements (it is very likely that it causes parasitic condensation) we found it necessary to clean the apparatus from time to time. The procedure used was similar to that described in an earlier paper (1). Here the apparatus was washed with a solution of  $KMnO_A$  in dilute (~5%) KOH until no further reduction to green MnO $_{4}^{-}$  was observed in the effluent. To remove the precipitated MnO, warm oxalic acid solution was used. After rinsing with large quantities of doubly distilled water the system was pumped to dryness. Although this procedure was completely satisfactory for VPIE measurements of hydrocarbons it did not bring similar results with H2O-D2O.

This problem could be solved by an additional washing with NH,OH solution.

It is mentioned here that the removal of the adsorbed water and air from the apparatus took 2-3 days even if the apparatus was heated to 100 °C and the vacuum system run continuously. Because of this, we always degassed the samples outside the apparatus (by many freeze-pump-thaw-freeze cycles) and only after complete degassing (controlled with the manometer) did we distil them into the equilibrium chambers.

# 3. RESULTS AND DISCUSSION

The isotopic pressure differences and the total pressures of the  $\rm H_2O$  sample of the equimolar mixture system are presented in Table I; while those of the pure  $\rm H_2O-D_2O$  system in Table II.

The tabulated isotopic pressure differences are (linearly) extrapolated values: those in Table I from the experimental 49.936 at % D to 50%, and those in Table II from 99.815 at % D to 100%. In the case of the mixture system we took 198 data, for the pure  $D_2O$  159 data. The corrected data were fitted by the nonlinear least squares technique to the following equation:

$$\ln(p_{H}/p_{D}) = A_{1} + A_{2}/T + A_{3}/T^{2}$$
 (1)

where  $\rm p_H$  is the vapour pressure of the  $\rm H_2O$  sample and  $\rm p_D$  is the vapour pressure either of the pure  $\rm D_2O$  or the equimolar  $\rm H_2O-D_2O$  mixture.

The parameters of Eq.(1) together with the corresponding error matrixes and standard deviations [10,11] are given in Table III.

To check the reliability of the present VPIE measurements we compared our data on the pure  ${\rm H_2O-D_2O}$  system with those from the literature. Namely the VPIE of this system is known very accurately in a wide range of temperatures in contrast to the data on the equimolar mixture system [5,6]. The several VPIE measurements on the pure  ${\rm D_2O}$  have been reviewed by Jancso and Van Hook [12] and we used their equation for comparison. Our

data in the temperature range 5 to 85 °C lie, on average, 0.5 rel.% higher; we regard this as a satisfactory agreement. Naturally we prefer to use our values in the analysis of the mixture data since both measurements have been carried out on the same apparatus.

The discussion of the ideality of the equimolar H<sub>2</sub>O-D<sub>2</sub>O mixture system, using the present experimental results, has been prepared as a subsequent publication [13].

Vapour pressures of  $\rm H_2O$  and vapour pressure differences between  $\rm H_2O$  and the equimolar  $\rm H_2O-D_2O$  mixture (50 at % D)

t/°c	PH2O/kPa	$\Delta p/kPa = p_{H_2}O^{-p}mixture$	t/°c	P <sub>H2</sub> O/kPa	$= p_{H_2O}^{\Delta p/kPa} =$
14.35	1.6342	0.1331	9.31	1.1719	0.1015
20.78	2.4532	0.1835	10.57	1.2750	0.1013
26.89	3.5429	0.2471	11.88	1.3908	0.1164
27.10	3.5861	0.2471	13.19	1.5158	0.1246
32.96	5.0209	0.3234	13.96	1.5939	0.1299
33.04	5.0429	0.3248	14.48	1.6479	0.1331
37.28	6.3748	0.3878	14.99	1.7035	0.1331
37.44	6.4288	0.3901	15.51	1.7608	0.1404
41.27	7.8943	0.4562	15.97	1.8137	0.1438
41.48	7.9812	0.4596	16.82	1.9145	
45.21	9.6932	0.5321	17.31	1.9748	0.1499
45.40	9.7840	0.5355	17.79		0.1538
49.89	12.273	0.6343	18.46	2.0367	0.1579
50.07	12.273	0.6384	1		0.1634
30.07	12.303	0.0304	18.90 25.83	2.1832 3.3285	0.1668
15.74	1.7871	0.1421	26.82	3.5268	0.2349
17.46	1.9942	0.1552	35.84	5.8891	0.2452
23.85	2.9565	0.2124	36.74	6.1887	0.3656
24.49	3.0731	0.2124	43.68	8.9568	0.3794 0.5016
29.27	4.0685	0.2738	44.49	9.3374	0.5158
29.91	4.2226	0.2813	50.88	12.888	0.6564
38.19	6.6957	0.4018	51.37	13.205	0.6675
39.38	7.1388	0.4161	56.29	16.746	0.7943
54.28	15.216	0.7396	56.81	17.164	0.8070
60.51	20.402	0.9134	60.69	20.574	0.9234
60.79	20.402	0.9210	61.16	21.023	0.9360
66.30	26.511	1.099	61.26	21.124	0.9395
66.54	26.788	1./107	64.50	24.464	1.045
71.27	32.919	1.281	64.92	24.926	1.043
71.55	33.328	1.291	71.01	32.552	1.273
76.37	40.824	1.483	71.24	32.883	1.280
76.55	41.136	1.488	74.41	37.612	1.406
79.59	46.597	1.621	74.59	37.902	1.411
79.78	46.945	1.635	77.11	42.082	1.514
			77.28	42.401	1.523
			78.31	44.219	1.570
			79.36	46.152	1.614

Table I continued

t/°c	PH2O/kPa	Δp/kPa = = p <sub>H2</sub> O <sup>-p</sup> mixture	t/°c	PH20/kPa	Δp/kPa = = p <sub>H2</sub> 0 <sup>-p</sup> mixture
81.09	49.498	1.690	79.31	46.054	1.613
81.19	49.707	1.695	79.46	46.349	1.620
83.06	53.546	1.780	79.54	46.498	1.623
84.37	56.398	1.836	80.59	48.514	1.676
85.00	57.812	1.871	80.96	49.237	1.692
86.73	61.856	1.957	81.46	50.233	1.713
86.97	62.425	1.968	81.69	50.711	1.722
		MARKET THE REAL PROPERTY.	81.88	51.085	1.729
17.90	2.0500	0.1596	83.03	53.491	1.785
18.62	2.1449	0.1656	83.69	54.900	1.820
19.26	2.2328	0.1708	84.34	56.340	1.851
26.74	3.5108	0.2437	84.97	57.753	1.878
29.99	3.5645	0.2464	85.13	58.110	1.885
42.62	8.4740	0.4814	85.37	58.651	1.894
42.98	8.6363	0.4885			
49.22	11.868	0.6213	14.02	1.5992	0.1312
49.84	12.242	0.6340	15.71	1.7841	0.1430
55.82	16.377	0.7841	16.59	1.8860	0.1494
55.87	16.417	0.7861	17.44	1.9909	0.1558
56.00	16.519	0.7881	18.29	2.1003	0.1626
56.89	17.228	0.8125	20.01	2.3388	0.1766
56.96	17.291	0.8143	20.86	2.4649	0.1838
56.99	17.313	0.8154	21.38	2.5441	0.1896
58.16	18.294	0.8499	21.79	2.6091	0.1932
58.27	18.384	0.8526	29.09	4.0262	0.2733
64.97	24.984	1.066	29.99	4.2414	0.2841
62.28	25.337	1.075	31.26	4.5596	0.2997
65.49	25.574	1.080	36.74	6.1887	0.3799
67.68	28.181	1.151	37.00	6.2767	0.3840
67.74	28.246	1.153	42.13	8.2581	0.4725
73.02	35.474	1.356	47.34	10.804	0.5783
73.31	35.909	1.366	47.63	10.961	0.5840
75.56	39.469	1.458	50.75	12.806	0.6558
75.90	40.033	1.470	51.06	13.004	0.6627
76.24	40.603	1.483	51.27	13.138	0.6672
76.37	40.824	1.487	55.19	15.895	0.7705
78.31	44.219	1.574	55.61	16.215	0.7793
78.75	45.032	1.593	55.77	16.334	0.7842
78.99	45.468	1.601	62.27	21.124	0.9430

Table I continued

t/°C	PH2O/kPa	bp/kPa =	t/°c	P <sub>H2</sub> O/kPa	$= p_{\text{H}_2\text{O}}^{\text{Ap/kPa}} =$
61.58	21.429	0.9511	19.55	2.2725	0.1735
68.47	29.165	1.182	20.01	2.3388	0.1778
68.81	29.601	1.192	49.37	11.960	0.6245
68.99	29.838	1.200	50.05	12.369	0.6390
72.29	34.386	1.323	50.31	12.529	0.6442
72.47	34.581	1.330	54.10	15.083	0.7381
76.13	40.427	1.480	54.26	15.196	0.7421
76.32	40.736	1.487	56.99	17.313	0.8160
79.46	46.349	1.619	57.64	17.852	0.8323
79.62	46.646	1.625	60.61	20.501	0.9194
79.75	46.646	1.625	60.93	20.798	0.9290
81.14	49.602	1.692	64.06	23.981	1.030
81.35	50.022	1.700	64.34	24.293	1.037
		The state of the s	67.37	27.795	1.142
7.98	1.0706	0.0948	67.74	28.246	1.179
8.87	1.1378	0.0995	70.22	31.471	1.245
9.72	1.2047	0.1039	70.85	32.333	1.267
10.55	1.2728	0.1088	73.67	36.469	1.375
11.75	1.3790	0.1158	77.11	42.082	1.514
12.29	1.4290	0.1191	77.34	42.493	1.523
13.11	1.5082	0.1242	79.72	46.845	1.627
14.14	1.6126	0.1312	79.88	47.145	1.632
14.86	1.6894	0.1361	82.08	51.515	1.732
15.69	1.7812	0.1420	82.37	52.112	1.749
16.59	1.8866	0.1486	83.79	55.128	1.814
17.44	1.9909	0.1552	84.84	57.456	1.861
18.29	2.1003	0.1620			

Vapour pressures of  ${\rm H_2O}$  and vapour pressure differences between  ${\rm H_2O}$  and  ${\rm D_2O}$  (100 at % D)

t/°c	PH20/kPa	$^{\Delta p/kPa} = p_{H_2O} - p_{D_2O}$	t/°c	PH2O/kPa	$^{\Delta p/kPa} = p_{H_2O}^{-p} p_{D_2O}$
17.54	2.0039	0.3020	51.79	13.478	1.320
20.84	3.3285	0.4511	51.89	13.547	1.327
32.45	4.8770	0.6088	52.07	13.668	1.331
38.01	6.6304	0.7721	52.15	13.720	1.334
42.62	8.4740	0.9291	57.28	17.548	1.601
42.73	8.5201	0.9317	57.49	17.722	1.611
47.24	10.747	0.4472	61.08	20.948	1.818
47.24	10.747	1.114	61.63	21.480	1.849
55.51	16.135	1.503	61.89	21.738	1.864
56.24	16.704	1.540	62.10	21.946	1.877
62.18	22.025	1.882	65.41	25.485	2.088
62.36	22.209	1.891	65.65	25.753	2.107
68.91	29.736	2.320	65.96	26.114	2.126
68.97	29.804	2.326	66.14	26.327	2.138
73.28	35.869	2.643	70.74	32.188	2.461
73.34	35.949	2.648	71.06	32.625	2.482
			71.40	33.104	2.506
13.94	1.591	0.2486	74.54	37.819	2.746
14.74	1.6755	0.2597	75.03	38.616	2.779
15.99	1.8167	0.2772	75.66	39.642	2.835
27.77	3.7298	0.4928	78.12	43.888	3.027
27.98	3.7750	0.4970	78.39	44.362	3.049
33.40	5.1462	0.6351	78.52	44.600	3.060
33.56	5.1910	0.6398	80.38	48.105	3.215
33.71	5.2362	0.6432	80.69	48.720	3.242
39.92	7.3494	0.8359	81.06	49.445	3.271
40.03	7.3902	0.8389	82.87	53.157	3.433
40.06	7.4004	0.8400	83.16	53.770	3.456
45.73	9.9545	1.052	88.62	66.536	4.004
45.91	10.047	1.058	88.70	66.737	4.014
45.99	10.087	1.062			
46.07	10.128	1.065	7.75	1.0538	0.1776
51.19	13.088	1.291	8.08	1.0781	0.1806
51.42	13.239	1.304	8.77	1.1300	0.1879
51.29	13.155	1.297	9.24	1.1658	0.1927
51.53	13.307	1.308	9.64	1.1985	0.1971
51.66	13.392	1.314	10.29	1.2512	0.2043

Table II continued

t/°c	PH2O/kPa	$= \frac{\Delta p/kPa}{P_{H_2}O^{-p}D_2O}$	t/°c	PH2O/kPa	Δp/kPa = = p <sub>H2</sub> O <sup>-p</sup> D <sub>2</sub> O
10.83	1.2970	0.2105	8.11	1.0800	0.1821
11.86	1.3884	0.2225	9.19	1.1618	0.1936
12.37	1.4363	0.2288	9.67	1.2005	0.1987
13.60	1.5570	0.2441	10.14	1.2383	0.2039
14.35	1.6342	0.2544	10.14	1.2728	0.2086
15.12	1.7176	0.2649	11.11	1.3216	0.2151
16.59	1.8866	0.2861	11.39	1.3466	0.2168
17.15	1.9556	0.2941	11.60	1.3651	0.2207
18.03	2.0666	0.3081	12.16	1.4170	0.2274
19.52	2.2689	0.3319	12.65	1.4632	0.2334
20.68	2.4377	0.3516	13.17	1.5132	0.2403
22.95	2.7998	0.3929	13.68	1.5648	0.2466
24.26	3.0306	0.4182	14.25	1.6234	0.2542
24.52	3.0778	0.4238	14.76	1.6783	0.2609
24.88	3.1449	0.4309	15.25	1.7319	0.2680
30.02	4.2477	0.5460	15.68	1.7812	0.2741
30.20	4.2920	0.5502	16.25	1.8468	0.2825
35.39	5.7482	0.6909	16.69	1.8990	0.2888
35.65	5.8308	0.6985	17.93	2.0533	0.3074
40.78	7.6913	0.8641	18.11	2.0767	0.3106
44.49	9.3374	1.001	18.31	2.1037	0.3125
44.57	9.3750	1.004	30.74	4.4273	0.5635
48.05	11.192	1.147	30.92	4.4732	0.5678
48.12	11.236	1.151	36.22	6.0160	0.7167
52.73	14.108	1.361	41.25	7.8836	0.8803
56.06	16.560	1.533	41.27	7.8944	0.8804
56.11	16.601	1.534	45.32	9.7450	1.035
60.98	20.848	1.810	45.42	9.797	1.037
61.11	20.973	1.819	50.15	12.433	1.245
65.70	25.813	2.107	50.23	12.481	1.248
65.76	25.873	2.109	50.46	12.626	1.257
69.36	30.316	2.359	54.31	15.235	1.447
69.41	30.385	2.362	54.88	15.659	1.477
72.24	34.310	2.573	55.32	15.995	1.498
73.23	35.790	2.644	59.75	19.701	1.744
76.89	41.719	2.934	59.99	19.917	1.755
77.21	42.264	2.958	63.06	22.931	1.945
81.54	50.392	3.321	63.32	23.203	1.957
81.85	51.031	3.348	66.17	26.358	2.151
85.92	59.928	3.718	67.24	27.284	2.219

Table II continued

PH2O/kPa	$^{\Delta p/kPa} = ^{p_{H_2}0^{-p}D_2^0}$
27.699	2.222
31.329	2.419
31.613	2.433
36.068	2.665
	27.699 31.329 31.613

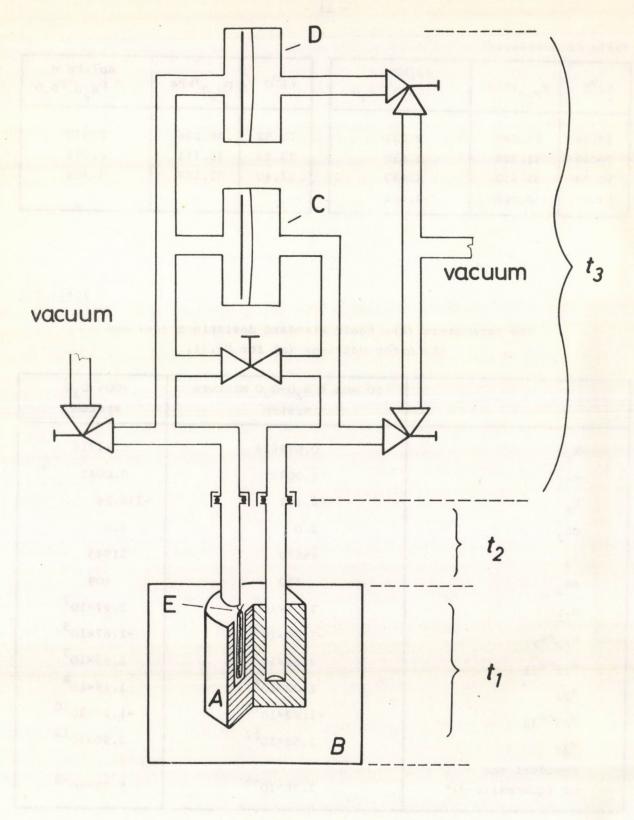
t/°c	PH2O/kPa	$\Delta p/kPa = p_{H_2O}^{-p} p_{D_2O}^{-p}$
73.52	36.228	2.670
73.83	36.711	2.691
82.40	52.167	3.305

Table III

The parameters (A), their standard deviations ( $\sigma$ A) and the error matrixes (a) for Eq.(1)

	50 mol % H <sub>2</sub> O-D <sub>2</sub> O mixture system	100% D <sub>2</sub> O system
A <sub>1</sub>	0.076624	0.14716
σA <sub>1</sub>	0.0031	0.0041
A <sub>2</sub>	-88.161	-173.28
σA <sub>2</sub>	2.0	2.6
A <sub>3</sub>	25972	51545
σA <sub>3</sub>	312	409
a <sub>11</sub>	2.51×10 <sup>2</sup>	2.97×10 <sup>2</sup>
a <sub>12</sub> =a <sub>21</sub>	-1.60×10 <sup>5</sup>	-1.87×10 <sup>5</sup>
a <sub>13</sub> =a <sub>31</sub>	2.54×10 <sup>7</sup>	2.93×10 <sup>7</sup>
a <sub>22</sub>	1.02×10 <sup>8</sup>	1.18×10 <sup>8</sup>
a <sub>23</sub> =a <sub>32</sub>	-1.62×10 <sup>10</sup>	-1.85×10 <sup>10</sup>
<sup>a</sup> 33	2.58×10 <sup>12</sup>	2.90×10 <sup>12</sup>
residual sum of squares/(n-3)*	3.78×10 <sup>-8</sup>	5.77×10 <sup>-8</sup>

<sup>\*</sup>n is the number of experimental data points



 $t_3 > t_2 > t_1$ 

Fig. 1
Apparatus for measuring vapour pressure isotope effect

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