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EQUIMOLAR $\text{H}_2\text{O}-\text{D}_2\text{O}$ MIXTURE

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EQUIMOLAR H₂O-D₂O MIXTURE

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ABSTRACT

New high precision vapour pressure data on equimolar $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures are analysed. The results show that the $\text{H}_2\text{O}-\text{HDO}-\text{D}_2\text{O}$ liquid mixture can be considered as an ideal solution within the limits of the presently available data. The present investigation supports the earlier conclusion that the law of the geometric mean for the vapour pressure isotope effect in the series H_2O , HDO and D_2O is not obeyed.

АННОТАЦИЯ

Были проанализированы новые высокоточные данные по давлению пара эквимольной смеси $\text{H}_2\text{O}-\text{D}_2\text{O}$. Результаты показывают, что жидкая смесь $\text{H}_2\text{O}-\text{HDO}-\text{D}_2\text{O}$ может считаться идеальной в пределах точности измерений экспериментальных данных. Исследования подтверждают сделанное ранее предположение о том, что к давлению пара молекул H_2O , HDO и D_2O не приложимо правило средней геометрической величины.

KIVONAT

Ekvimoláris $\text{H}_2\text{O}-\text{D}_2\text{O}$ elegyek gőznyomására rendelkezésre álló új, nagypontosságú adatokat analizáltuk. Az eredmények azt mutatják, hogy a $\text{H}_2\text{O}-\text{HDO}-\text{D}_2\text{O}$ folyadék elegy ideálisnak tekinthető a kísérleti adatok mérési pontosságán belül. A vizsgálatok alátámasztják azt a korábbi következtetést is, mely szerint a H_2O , HDO és D_2O molekulák gőznyomására nem érvényes a geometriai közép szabálya.

INTRODUCTION

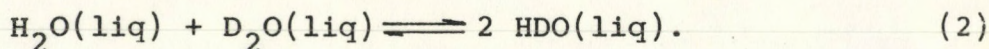
Isotopic mixtures have for some while been considered as the best examples of ideal solutions therefore the study of the deviation of such solutions from the ideal behaviour seems to be especially interesting. Precise vapour pressure measurements on isotopic mixtures with known isotopic composition represent one of the most convenient ways to carry out such investigations. The results of the recent determination of the vapour pressures of equimolar solutions of C_6H_6 and C_6D_6 and of C_6H_{12} and C_6D_{12} have shown that these mixtures deviate from ideality [1]. The excess thermodynamic properties of these solutions were interpreted in terms of the molar volume isotope effect and the pressure dependence of the molecular vibrational frequencies [2,3].

The different experimental techniques which have been used for determining the eventual nonideal behaviour of H_2O - D_2O liquid mixtures were summarized by Phutela and Fenby [4] and Van Hook [5]. These techniques include the measurement of the vapour pressures of H_2O - D_2O mixtures [6-8], ebulliometric measurements [9] and the determination of the freezing points of the mixtures [10]. The latter data have been considered in detail by Van Hook [11] who concluded that the H_2O - D_2O solutions do not deviate from the ideal behaviour and by using this assumption the ratio

$$r = \ln \left(\frac{P_{H_2O}}{P_{D_2O}} \right) / \ln \left(\frac{P_{H_2O}}{P_{HDO}} \right) \quad (1)$$

was evaluated from the literature data on vapour pressure isotope effects [13-15] and found to be 1.91 ± 0.03 [12]. The extension of the data base to the boiling points [9] and freezing points [10] of mixtures of the isotopic waters resulted in a constant, temperature independent, r value (1.91 ± 0.02) between 0 and $200^\circ C$ over a wide HOD concentration range [5].

The H₂O-D₂O liquid mixtures should be treated as three component systems due to the equilibrium



Phutela and Fenby [4], by using vapour pressure isotope effect data for HDO and D₂O and assuming the H₂O-HDO-D₂O liquid mixtures to be ideal, evaluated deviations from Raoult's law. The negative deviations found mean that the vapour pressure of the mixture is higher if it is considered as a two component system instead of a three component system.

New high precision vapour pressure data on equimolar H₂O-D₂O mixtures obtained in this laboratory for a wide temperature range [16] make it possible to reinvestigate the problem of the ideal behaviour of this solution.

In this paper the following definition of an ideal mixture is used: it is a mixture in which the chemical potential of component *i* is given by the equation

$$\mu_i(p, T, x_i) = \mu_i^{\circ}(p, T) + RT \ln x_i \quad (3)$$

where $\mu_i^{\circ}(p, T)$ is the chemical potential of the pure liquid component *i* at the same pressure and temperature as the mixture being studied and x_i is the mole fraction of component *i* in the liquid mixture [17]. (This definition leads to Raoult's law if the vapour is a perfect gas and the molar volumes of the liquids are negligibly small.)

DISCUSSION

The details of the experimental determination of the vapour pressure of the equimolar H₂O-D₂O mixture are given elsewhere [16]. A summary of the experimental data obtained is given in *Table I*.

Let us consider a liquid mixture at temperature *T*, formed from 0.5 mol of H₂O and 0.5 mol of D₂O; then the equilibrium mixture will contain 2*s* mol of HDO, (0.5-*s*) mol of D₂O and (0.5-*s*) mol of H₂O. The value of *s* can be obtained from the equilibrium constant of Eq.(2) (K_{liq}). The vapour pressure of an

Table I

The values of $\ln(p_{\text{H}_2\text{O}}/p_{\text{mixture}})$ and $\ln(p_{\text{H}_2\text{O}}/p_{\text{D}_2\text{O}})$ calculated from the least-squares fit equations of the experimental data [16]

t (°C)	$\ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{D}_2\text{O}}}$	$\ln \frac{p_{\text{H}_2\text{O}}}{p_{\text{mixture}}}$ ^{a)}	$p_{\text{H}_2\text{O}}$ [18] (kPa)	$p_{\text{H}_2\text{O}} - p_{\text{mixture}}$ (kPa)
0	0.20362 ^{c)}	0.10196 ^{d)}	0.6106 (4.580) ^{b)}	0.0592 (0.444)
5	0.19041	0.09536	0.8718 (6.539)	0.0793 (0.595)
10	0.17809	0.08921	1.2271 (9.204)	0.105 (0.785)
15	0.16659	0.08346	1.7041 (12.782)	0.1365 (1.024)
20	0.15585	0.07810	2.3370 (17.529)	0.1756 (1.317)
25	0.14582	0.07309	3.1667 (23.752)	0.2232 (1.674)
30	0.13643	0.06841	4.2426 (31.822)	0.2805 (2.104)
35	0.12766	0.06404	5.6231 (42.177)	0.3488 (2.616)
40	0.11944	0.05994	7.3771 (55.333)	0.4292 (3.219)
45	0.11174	0.05610	9.5848 (71.892)	0.5229 (3.922)
50	0.10453	0.05251	12.3387 (92.548)	0.6312 (4.735)
55	0.09778	0.04915	15.7452 (118.099)	0.7551 (5.664)
60	0.09144	0.04600	19.9252 (149.451)	0.8957 (6.718)
65	0.08550	0.04304	25.0150 (187.628)	1.054 (7.904)
70	0.07993	0.04027	31.1681 (233.780)	1.230 (9.227)
75	0.07469	0.03767	38.5552 (289.188)	1.425 (10.69)
80	0.06978	0.03523	47.3658 (355.273)	1.640 (12.30)
85	0.06517 ₅	0.03294	57.8086 (433.600)	1.873 (14.05)
90	0.06085	0.03079	70.1128 (525.889)	2.126 (15.95)

a) $p_{\text{H}_2\text{O}}$, $p_{\text{D}_2\text{O}}$ and p_{mixture} represent vapour pressures of H_2O , D_2O and equimolar $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixture, respectively.

b) The values in parentheses are given in mmHg.

c) The standard deviation of the calculated values is $\pm 3 \times 10^{-5}$.

d) The standard deviation of the calculated values is $\pm 2 \times 10^{-5}$.

ideal liquid mixture (p) in equilibrium with a vapour phase which can be considered as an ideal mixture of imperfect gases is given by [17]

$$\begin{aligned}
 p = & x_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}} \exp \frac{(p-p_{\text{H}_2\text{O}})(V_{\text{H}_2\text{O}}-B_{\text{H}_2\text{O}})}{RT} + \\
 & + x_{\text{HDO}} p_{\text{HDO}} \exp \frac{(p-p_{\text{HDO}})(V_{\text{HDO}}-B_{\text{HDO}})}{RT} + \\
 & + x_{\text{D}_2\text{O}} p_{\text{D}_2\text{O}} \exp \frac{(p-p_{\text{D}_2\text{O}})(V_{\text{D}_2\text{O}}-B_{\text{D}_2\text{O}})}{RT}
 \end{aligned} \quad (4)$$

where in the case of equimolar $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixture $x_{\text{H}_2\text{O}} = x_{\text{D}_2\text{O}} = 0.5-s$, $x_{\text{HDO}} = 2s$, p_i and V_i are the respective vapour pressures and molar volumes of the pure liquids i at temperature T ; and B_i is the second virial coefficient.

In order to estimate the contributions of different terms in Eq.(4) to the vapour phase nonideality, calculations were carried out for $t = 75^\circ\text{C}$ where the effect of the nonideal behaviour of the vapour phase might be expected to be significant. The data employed in the calculations are collected in *Table II*.

The second virial coefficient data need some comments. The isotope effect on the second virial coefficient of the D_2O vapour has been reported by Kell, McLaurin and Whalley [21] for the temperature range 150 to 500°C . The data show a smooth decrease in the difference $|(B_{\text{H}_2\text{O}}-B_{\text{D}_2\text{O}})/B_{\text{H}_2\text{O}}|$ from 1.3% at 200°C to 0.1% at 450°C . Gupta, Jain and Nanda [22] carried out calculations on $B_{\text{D}_2\text{O}}$ using p - T data along the saturation line for the temperature range 70 - 160°C . The values were found to be consistently more negative than those for ordinary water and $|\Delta B/B_{\text{H}_2\text{O}}|$ was found to decrease from 12.4% at 70°C to about 2% at 160°C . They concluded that the principle of corresponding states with respect to the second virial coefficients for the two waters is obeyed if $V_{\text{CH}_2\text{O}}$ and $T_{\text{CH}_2\text{O}}$, and $0.983 V_{\text{CD}_2\text{O}}$ and $1.017 T_{\text{CD}_2\text{O}}$ - where V_c and T_c are the critical volume and temperature, respectively - are used as reducing parameters. On the other hand Lagutkin and Dergachev [23] arrived at the conclusion (using a different set of p - V - T data in their calculation) that the law of corresponding states is obeyed with the reduced variables V/V_c and T/T_c . However, the use of the latter authors' results is made difficult by the discrepancies between the data shown on their graph and those obtained by using the equation formulated for the description of the data.

Input data used in the estimation of the effect of the nonideality of the vapour phase

$$t = 75 \text{ } ^\circ\text{C}$$

$$P_{\text{H}_2\text{O}} = 38.5552 \text{ kPa [18]; } P_{\text{D}_2\text{O}} = 35.7803 \text{ kPa [16]; } P_{\text{HDO}} = 37.0766 \text{ kPa}^{\text{a)}$$

$$(289.188) \quad (268.374)^{\text{e)}$$

$$(278.097)$$

$$x_{\text{D}_2\text{O}} = x_{\text{H}_2\text{O}} = 0.25304; \quad x_{\text{HDO}} = 0.49392^{\text{b)}$$

$$V_{\text{H}_2\text{O}} = 18.475 \text{ cm}^3 \text{ mol}^{-1}; \quad V_{\text{D}_2\text{O}} = 18.513 \text{ cm}^3 \text{ mol}^{-1} \text{ [19]}$$

$$M_{\text{H}_2\text{O}} = 18.0106 \text{ gmol}^{-1}; \quad M_{\text{D}_2\text{O}} = 20.0231 \text{ gmol}^{-1}$$

$$B_{\text{H}_2\text{O}} = -599 \text{ cm}^3 \text{ mol}^{-1}^{\text{c)}$$

$$-540 \text{ cm}^3 \text{ mol}^{-1}^{\text{d)}$$

$$-578 \text{ cm}^3 \text{ mol}^{-1} \text{ [22]}$$

$$\frac{B_{\text{H}_2\text{O}} - B_{\text{D}_2\text{O}}}{B_{\text{H}_2\text{O}}} \times 100 = 11.2 \text{ [22]}$$

a) This value was obtained by using $r = 1.91$.

b) $K_{\text{liq}} = 3.81$ (see in the text).

c) Calculated from the equation $B(\text{cm}^3 \text{ g}^{-1}) = 1.89 - \frac{2641.6}{T} \times \exp \frac{1.858 \times 10^5}{T^2}$ given in [20].

c) Extrapolated value obtained from the data given in Table II of [21].

e) The values in parentheses are given in mmHg.

If the equimolar liquid mixture of H₂O and D₂O obeyed Raoult's law the vapour pressure of the mixture could be given as

$$p = x_{\text{H}_2\text{O}} \times p_{\text{H}_2\text{O}} + x_{\text{D}_2\text{O}} \times p_{\text{D}_2\text{O}} + x_{\text{HDO}} \times p_{\text{HDO}}. \quad (5)$$

Since the differences between Eqs. (4) and (5) are small, we can, in very good approximation, substitute p from Eq. (5) into the nonideal vapour phase correction terms in Eq. (4). The partial vapour pressures obtained from Eq. (4) are then compared with those given by Raoult's law /Eq. (5)/ and the results are summarized in *Table III*. It can be seen that the corrections due to the nonideality of the vapour phase can be completely neglected since the precision of the determination of the vapour pressure difference between the equimolar H₂O-D₂O mixture and the pure H₂O is about ± 1.3 - 2.7 Pa (± 0.01 - 0.02 mmHg). Therefore Eq. (5) can be used instead of Eq. (4) in the present case and any deviation from the ideal solution behaviour can be observed as a deviation from Raoult's law.

Next, the effect of the equilibrium constant for Eq. (2) will be investigated. The available literature data for K_{liq} and K_{gas} at different temperatures are collected in *Table IV*. The vapour pressure difference between the pure H₂O and the equimolar H₂O-D₂O mixture (Δp) is given by

$$\Delta p = p_{\text{H}_2\text{O}} - p = p_{\text{H}_2\text{O}} \left[1 - 2s \left(\frac{p_{\text{D}_2\text{O}}}{p_{\text{H}_2\text{O}}} \right)^{1/r} - (0.5-s) \left(\frac{p_{\text{D}_2\text{O}}}{p_{\text{H}_2\text{O}}} - 1 \right) \right] \quad (6)$$

where the values for s are obtained from K_{liq} . The calculations with different values of K_{liq} and with the data given in *Table I* were performed for $t = 75$ °C and the results are shown in *Table V*. The values obtained for Δp demonstrate that they are insensitive to the value selected for K_{liq} - at least within the limits of experimental error.

Equation (6) can be written as

$$\Delta p = x_{\text{D}_2\text{O}} (p_{\text{H}_2\text{O}} - p_{\text{D}_2\text{O}}) + x_{\text{HDO}} (p_{\text{H}_2\text{O}} - p_{\text{HDO}}) \quad (7)$$

which is convenient for estimating the influence of the precision of the measurement on the calculations.

Table III

Comparison of partial vapour pressures p_i^* and p_i^{**} obtained with and without nonideal vapour phase correction terms, respectively

Assumption		$P_{H_2O}^* - P_{H_2O}^{**}$	$P_{D_2O}^* - P_{D_2O}^{**}$	$P_{HDO}^* - P_{HDO}^{**}$	$\Sigma p_i^* - \Sigma p_i^{**}$
		(Pa)			
$B_{HDO} = B_{H_2O} = -599 \text{ cm}^3 \text{ mol}^{-1}$	$V_{HDO} = V_{H_2O}$	-2.9 ₉ (-0.022 ₄) ^{b)}	2.8 ₈ (0.021 ₆)	0.1 ₉ (0.001 ₄)	0.0 ₈ (0.000 ₆)
	$V_{HDO} = V_{D_2O}$	-2.9 ₉ (-0.022 ₄)	2.8 ₈ (0.021 ₆)	0.1 ₉ (0.001 ₄)	0.0 ₈ (0.000 ₆)
$B_{HDO} = 1.056 B_{H_2O}$	$V_{HDO} = V_{H_2O}$	-2.9 ₉ (-0.022 ₄)	2.8 ₈ (0.021 ₆)	0.2 ₀ (0.001 ₅)	0.0 ₉ (0.000 ₇)
$B_{H_2O} = B_{D_2O} = B_{HDO} = -599 \text{ cm}^3 \text{ mol}^{-1}$		-2.9 ₉ (-0.022 ₄)	2.6 ₀ (0.019 ₅)	0.1 ₉ (0.001 ₄)	0.2 ₀ (-0.001 ₅)
$B_{HDO} = B_{H_2O} = -540 \text{ cm}^3 \text{ mol}^{-1}$		-2.6 ₉ (-0.020 ₂)	2.6 ₀ (0.019 ₅)	0.1 ₆ (0.001 ₂)	0.0 ₇ (0.000 ₅)

$$a) p_{i, \text{Eq. (4)}}^* = x_i p_i \exp \frac{(p-p_i)(v_i - B_i)}{RT}; \quad p_{i, \text{Eq. (5)}}^{**} = x_i p_i$$

b) The values in parentheses are given in mmHg.

Table IV

The equilibrium constant of the reaction $\text{H}_2\text{O} + \text{D}_2\text{O} \rightleftharpoons 2\text{HDO}$

t (°C)	K_{gas}	K_{liq}
0	3.74± 0.02 [24] ^{a)}	3.78± 0.03 [12] ^{d)}
	3.83 [26-28] ^{b)}	
	3.75± 0.08 [25] ^{a)}	
20		3.94± 0.12 [29] ^{c)}
25	3.76± 0.02 [24]	3.78± 0.03 [12] 3.85± 0.03 [30] ^{e)}
	3.85 [26-28]	
	3.74± 0.07 [25]	
75	3.80± 0.04 [24]	3.81± 0.02 [12]
	3.90 [26-28]	

- a) Mass spectrometric determination.
- b) Theoretical calculation from spectroscopic data.
- c) Measured by NMR technique.
- d) Calculated by using K_{gas} [24] and vapour pressure isotope effect data.
- e) From measuring the fractionation factor for 1,3,5-trimethoxy benzene dissolved in water.

Table V

The influence of the value of the equilibrium constant (K_{liq})
on the Δp calculation

K_{liq} ^{a)}	Δp ^{b)} (kPa)
3.5	1.4316 (10.738) ^{c)}
3.7	1.4321 (10.742)
3.8	1.4325 (10.745)
3.9	1.4328 (10.747)
4.0	1.4331 (10.749)

a) $K_{liq} = \frac{(2s)^2}{(0.5-s)^2}$

b) $t = 75 \text{ }^\circ\text{C}; r = 1.91$

c) The values in parentheses are given in mmHg.

Since

$$P_{\text{HDO}} = \left(\frac{P_{\text{D}_2\text{O}}}{P_{\text{H}_2\text{O}}} \right)^{1/r} \times P_{\text{H}_2\text{O}} = \left(\frac{P_{\text{H}_2\text{O}} - \Delta p^*}{P_{\text{H}_2\text{O}}} \right)^{1/r} \times P_{\text{H}_2\text{O}} \approx \left(1 - \frac{1}{r} \frac{\Delta p^*}{P_{\text{H}_2\text{O}}} \right) P_{\text{H}_2\text{O}} \quad (8)$$

where $\Delta p^* = P_{\text{H}_2\text{O}} - P_{\text{D}_2\text{O}}$, if the uncertainty in the vapour pressure difference measurements is $\pm \delta^*$ then the corresponding uncertainties in P_{HDO} and in Δp will be $\pm \delta^*/r$ and $\sim \pm \delta^*/2$, respectively. In other words, even if the vapour pressure differences between the equimolar $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixture and H_2O , and between the pure H_2O and D_2O are determined on the same apparatus any systematic errors present will only partly cancel each other when the measured values of Δp are compared with those calculated from the right hand side of Eq.(6). On the other hand it is still advisable to employ $P_{\text{H}_2\text{O}} - P_{\text{D}_2\text{O}}$ values obtained on the same apparatus otherwise the errors arising from the calibration of different equipment might considerably shift the calculated Δp values and render the investigation of the validity of Raoult's law more difficult.

Although in the subsequent calculations a smoothed value of r , which was obtained by Van Hook [12] from experimental $\ln(P_{\text{H}_2\text{O}}/P_{\text{D}_2\text{O}})$ [14] and $\ln(P_{\text{H}_2\text{O}}/P_{\text{HDO}})$ [13] values, will be used and thus the error assigned to it are smaller than those of the individual $\ln(P_{\text{H}_2\text{O}}/P_{\text{HDO}})$ values, it is interesting to consider the importance attaching to the precision of the determination of P_{HDO} .

Taking Eq.(7) into consideration and that

$$\ln \frac{P_{\text{HDO}}}{P_{\text{H}_2\text{O}}} \approx \frac{P_{\text{HDO}} - P_{\text{H}_2\text{O}}}{P_{\text{H}_2\text{O}}} \quad (9)$$

and assuming that the error in $\ln(P_{\text{H}_2\text{O}}/P_{\text{HDO}})$ is $\pm \delta$ then the error in the calculated Δp value is $\pm \delta \times x_{\text{HDO}} \times P_{\text{H}_2\text{O}}$. Since the error of Majoube's measurement of the vapour pressure of HDO [13] is ± 0.001 in $P_{\text{H}_2\text{O}}/P_{\text{HDO}}$ for the temperature range $0-100^\circ\text{C}$ the uncertainty in the calculated Δp at 75°C can be given as .

$0.5 \times 38530 \text{ Pa} \times (\pm 0.001) = \pm 1.9 \text{ Pa} (\pm 0.14 \text{ mmHg})$; see also Fig.(1). This is considerably larger than the precision of the $p_{\text{H}_2\text{O}} - p_{\text{D}_2\text{O}}$ difference measurement.

The calculation of $p_{\text{H}_2\text{O}} - p$ values were carried out for the temperatures of 20, 50 and 75 °C by using Eq.(6) and $K_{\text{liq}} = 3.8$. The calculated and observed Δp values are compared in Fig. 1. The error bars attached to the measured data points correspond to about three standard deviations calculated from the fitting equations of paper [16] by using the law of propagation of errors [31, 32].

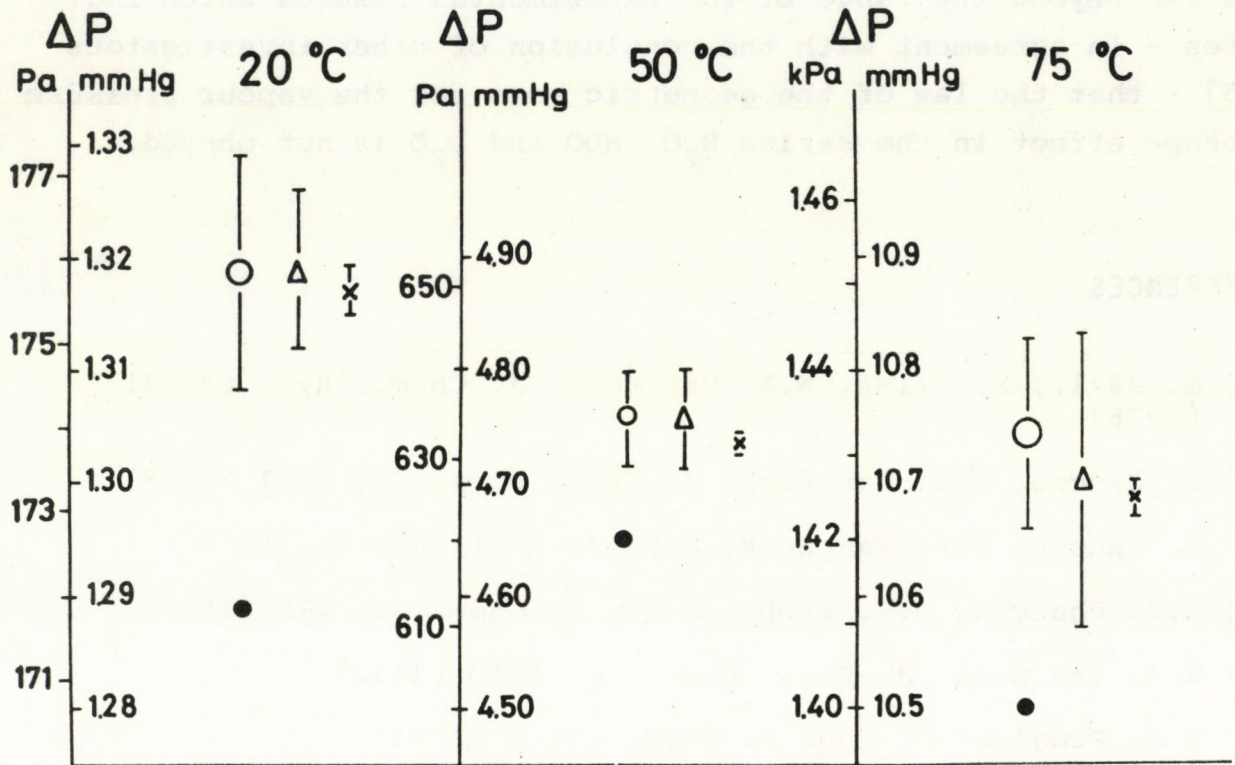


Fig. 1

Comparison of calculated and observed Δp ($p_{\text{H}_2\text{O}} - p_{\text{mixture}}$) values: \circ calculated with $r = 1.91$, the diameter is proportional to the error $\pm 1 \times 10^{-4}$ in $\ln(p_{\text{H}_2\text{O}}/p_{\text{D}_2\text{O}})$, the error bars correspond to an error of ± 0.03 in r ; \bullet calculated with $r = 2$; Δ calculated by using directly measured $\ln(p_{\text{HDO}}/p_{\text{H}_2\text{O}})$ data [13], the error bars correspond to ± 0.001 in $p_{\text{H}_2\text{O}}/p_{\text{HDO}}$; \times measured values with error bars corresponding to $\pm 1 \times 10^{-4}$ (0.6×10^{-4} at 75 °C) in $\ln(p_{\text{H}_2\text{O}}/p_{\text{mixture}})$

CONCLUSION

It can be seen from Fig. 1 that there are no significant differences between the measured and calculated Δp values, i.e. the vapour pressure of the equimolar mixture can be evaluated by using Eq.(4) or Eq.(5), which implies that the equimolar H_2O -HDO- D_2O liquid mixture does not deviate from the ideal behaviour within the limits of the presently available data. It is also clear that before any small deviation from the ideality can be detected the precision of the vapour pressure determination of HDO must be considerably improved. The values calculated with $r=2$ lie far beyond the range of the experimental results which indicates - in agreement with the conclusion of other investigators [15] - that the law of the geometric mean for the vapour pressure isotope effect in the series H_2O , HDO and D_2O is not obeyed.

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