Revista Mexicana de Física 30 no. 1 (1983) 63-82

THE VAPOUR PRESSURE OF PURE ORGANIC COMPOUNDS BY DYNAMIC EBULLIOMETRY

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(recibido noviembre 30, 1982; aceptado junio 30, 1983)

ABSTRACT

A dynamic ebulliometer has been used to measure vapour pressures of 2-propanol, 2,2,4-trimethylpentane, n-pentane, methanol, ethanol, acetone and benzene from approximately 26 to 78 kPa. The ebulliometer is similar to one reported in the literature although with modifications which make it original together with the auxiliary equipment and measuring technique. The values obtained in this work to test the ebulliometer are compared with data previously reported by other workers and the overall agreement is good. The experimental results were fitted to the Antoine equation and from it derived quantities were obtained for each of the seven substances studied.

RESUMEN

Un ebulliómetro dinámico ha sido utilizado para medir presiones de vapor de iso-propanol, 2,2,4-trimetilpentano, n-pentano, metanol, etanol, acetona y benceno desde 26 a 78 kPa. El ebulliómetro está basado en uno reportado en la literatura aunque incluye modificaciones que lo hacen original junto con el equipo auxiliar y la técnica de medición. Los vapores obtenidos en este trabajo se comparan con datos previamente reportados por otros grupos de investigación y la comparación es satisfactoria. Los resultados experimentales fueron ajustados a la ecuación de Antoine y a partir de ella se derivaron otras propiedades para cada una de las siete sustancias estudiadas.

1. INTRODUCTION

The knowledge of the thermodynamic properties of pure substances and mixtures is of great importance for the simulation, design and operation of many industrial processes. Further more, from a theoretical point of view those properties are used to test models of solutions and to give information on the molecular interactions.

TABLE I

Substance	n_D	(293.2° K)	n_D	(298.2° K)
	This work	Literature(1)	This work	Literature(1)
2 - propanol	1.3778	1.3772	1.3754	1.3753
2,2,4-trimethylpentane	1.3916	1.3915	1.3894	1.3890
n - pentane	1.3580	1.3575	1.3560	1.3547
methanol	1.3292	1.3286	1.3270	1.3266
ethanol	1.3619	1.3614	1.3602	1.3594
acetone	1.3595	1.3588(2)	1.3571	1.3570(2)
benzene	1.5140	1.5011	1.4987	1.4979

Table I. Refractive index at 293.2 and 2.98.2° K.

One of the thermodynamic properties of pure or single - component liquids that has been widely studied is the vapour pressure (p) as a function of temperature (T). Thus, we report a modified all-glass dynamic ebulliometer which has been tested measuring the vapour pressure of seven pure substances as a function of temperature. The approximate ranges of p for each substance in kPa (1 atmosphere = 101.325 kPa = 760 mmHg) are: 2-propanol 26 to 78, 2,2,4-trimethylpentane 19 to 78, n-pentane 26 to 124, methanol 26 to 78, ethanol 11 to 78, acetone 26 to 78 and benzene 16 to 78. Values obtained elswhere of the refractive indexes of these substances are presented in Table I.

2. APPARATUS

A circulating or dynamic ebulliometer similar to that described by Rogalski and co-workers$^{(3,4)}$ was used. Fig. 1 shows a schematic diagram of the ebulliometer. The main modification present in our ebulliometer is in the measurement of the equilibrium temperature between the vapour and liquid phases having the thermometer sealed in the ebulliometer with a threaded glass joint. This allows direct contact between the thermometer and the two phases thus the response is faster than using thermowells.

The working principle of the ebulliometer is now described. A stream of overheated liquid and vapour is continuosly generated with the aid of an electrical heater and pumped by the Cottrell pump A (see Fig. 1) towards the equilibrium chamber C where the thermometer is sealed with the joint D. A heating tape wound externally around the arm B prevents partial condensation of the vapour before reaching the equilibrium chamber. As part of the measuring technique the steady state corresponding to the thermodynamic equilibrium has to be established to carry out measurements of p-T and this was done in the present work by setting a value of drops between 70 to 90 as counted in the drop counter F. Finally the equilibrium temperature is determined in C as explained above from the contact between the thermometer and the liquid and vapour phases.

Mixing of the liquid phase from C and the condensed vapour phase from the condenser E is achieved in the devices I and J before the

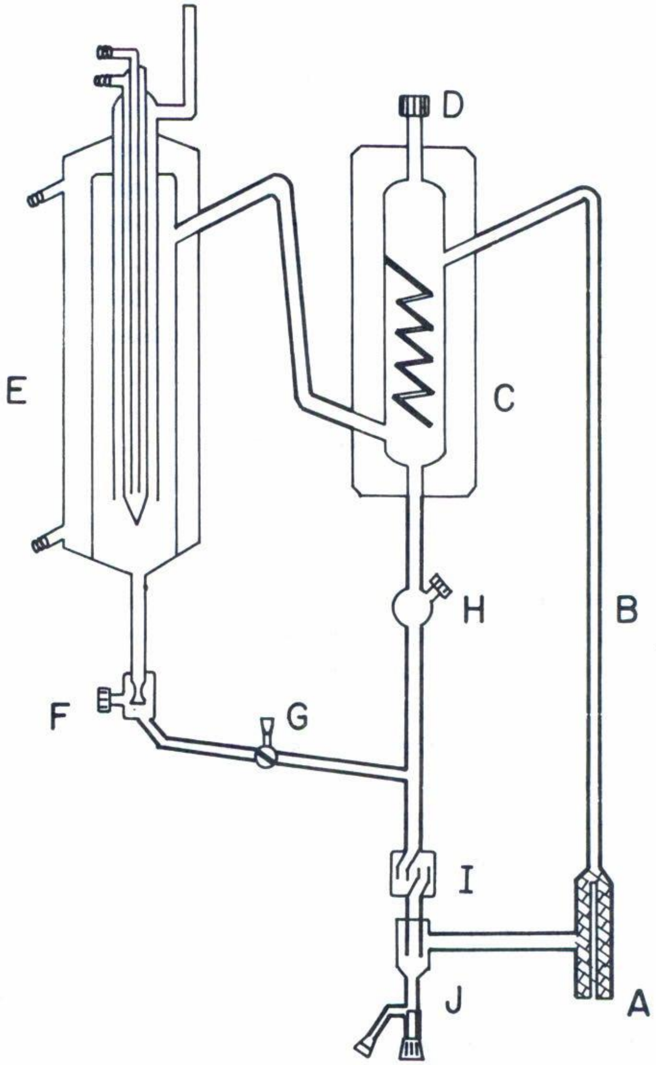

Fig. 1. The dynamic ebulliometer (see the text for description of the different parts).

liquid sample is again heated in A and the cycle started. The apparatus described here is also useful for the determination of the vapour - liquid equilibrium of mixtures(3,4,5) since both the liquid and vapour phases may be sampled to determine their composition through H and F, respectively.

3. AUXILIARY EQUIPMENT

The measurement of pressure was carried out with a mercury manometer used in the absolute fashion, i.e.,the reference limb was continuosly evacuated. The height of the mercury column was measured with a Gaertner cathetometer (model M-912) with a precision of ±0.01 mm. This type of manometer is well suited for pressure measurement up to approximately 130 kPa as discussed by Ambrose(6). A pennwalt manostat was used to control the pressure in the ebulliometer through a surge system composed amongst other things of two glass spheres of 20 l each thermally insulated. This surge system was connected to the ebulliometer and to the mercury manometer through a liquid nitrogen trap and connected to the pressure-vacuum system through the manostat. A direct-drive vacuum pump was used for measurements of vapour pressures below the atmospheric value whereas dry nitrogen was used as the pressurizing gas for pressures above the latter.

The measurement of equilibrium temperatures between the liquid and vapour in the equilibrium chamber was carried out with a Quartz Thermometer (Hewlett-Packard model 2804 A) with an absolute accuracy of ±0.04° K as reported by the makers for the temperature range studied in this work.

4. EXPERIMENTAL TECHNIQUE

The pure liquid to be studied was placed in the ebulliometer through the teflon valve G (see Fig. 1) until the liquid level was slightly above the mixing chamber I. After the cycle boiling-condensation-mixing-boiling has been established in the ebulliometer the stationary state has to be defined in terms of the pressure, temperature and amount of drops of condensate flowing through the drop counter F since these three quantities should be independent of time. According to the phase rule there exists only one degree of freedom for a system of one component and two phases, thus we decided to control the pressure within the ebulliometer in order to automatically define the thermodynamic state of the substance being studied, that is, the temperature is inmediately obtained for a given constant pressure. We have already mentioned in a previous section the amount of drops that we used as a criterion to establish the stationary state.

Several corrections have to be applied to the directly measured height of the mercury column in the manometer to finally obtain a value for the vapour pressure. These corrections are discussed in detail elsewhere(6,7), however, for completeness we give here the equation that was used to calculate values of vapour pressure from the manometric readings:

$$p/\text{mm Hg} = 0.9972 \ \ \Delta h(1 - 1.634\text{x}10^{-4} \ t) + Po \ , \qquad (1)$$

where Δh is the difference in height of the mercury columns between the measuring and reference limbs of the manometer, Po is the residual pressure in the reference limb of the manometer and t is the temperature of the manometer.

5. RESULTS AND DISCUSSION

The experimentally measured vapour pressures for each of the seven substances studied are listed in Tables II to VIII together with their residuals $p = (p_{exp} - p_{cal})$ from the Antoine equation:

$$\log_{10} \ (\rho/\text{kPa}) = A + B/\{(T/K) + C\} \quad . \qquad (2)$$

The constants of Eq. (2) were obtained from a least - square fit ad are given in Table IX.

The residuals in Table II to VIII correspond to temperature differences no greater than ±0.02°K indicating the goodness of the fit, furthermore the Δp values are randomly distributed.

Figures 2 to 8 show the pressure residuals Δp based on Eq. (2). Also included on these figures are the limits of pressure changes corresponding to changes in the temperature of ±0.02° K and ±0.04° K.

In order to compare with the present work we have used published values for each substance to calculate Δp where now p_{cal} are the values from Eq. (2) using the constants in Table IX and p_{exp} are the literature values. These residuals are also plotted in Figs. 2 to 8, from which it is observed that there is good agreement for each substance with the literature values. From this comparison is possible to give an accuracy for our measurements of ±0.05° K, which is in fact the largest deviation observed in each case and very close to the accuracy of the thermometer.

A further test on the quality of the results of this work and of the equation fitted to them may be carried out by calculating derived quantities such as the normal boiling temperature T_b, the slope of the saturation curve dp/dt and molar heats of vaporization ΔH. The normal boiling temperature obtained in this work for each substance is and extrapolation since the experimental values, with exception of n-pentane, were obtained below 101.325 kPa. Table X compares calculated boiling temperatures and dp/dt with literature values and the agreement is excellent in all cases. Differentiation of the Antoine equation together with the Clapeyron equation allows the calculation of the molar heats of vaporization ΔH:

$$\frac{2.303\ pB}{(T/K + C)}\ 2 = \frac{\Delta H}{\Delta V T} \quad , \qquad (3)$$

where ΔV is the difference of the molar volume of the vapour (V_V) and liquid (V_L) phases.

We have calculated V_L from density values from the literature$^{(17,18,19)}$ and V_V from the virial expantion. The second virial coefficient B(T) used in the latter equation was calculated from the correlation of Tarakad and Danner$^{(20)}$ in order to keep consistency.

Tabla XI compares calculated and experimental molar heats of vaporization at 298.2° K and at the boiling temperature for each substance. The relative error in each case is always smaller than 3% indicating the reliability of the calculated ΔH values from the fitted Antoine equation.

It is concluded that the ebulliometer and technique used in this study are very conyenient for determining vapour-liquid equilibrium data of pure substances in relatively short periods of time and in a relatively large range of pressure and temperature. It is clear, however, that the accuracy of the measurements may be further improved through a rigorous calibration of the quartz thermometer at several points of the temperature range used in this work.

TABLE II

T/K	p_{exp}/kPa	Δp/Pa	T/K	p_{exp}/kPa	Δp/Pa
325.42	26.419	-78	340.12	52.957	-22
327.39	29.152	-45	342.30	58.347	-22
329.06	31.659	- 9	343.25	60.904	45
330.77	34.462	82	344.26	63.625	20
332.28	36.912	-26	345.15	66.137	27
333.84	39.773	25	346.13	68.938	-27
335.19	42.310	-15	347.86	74.223	-36
336.57	45.151	46	349.08	78.190	- 5
337.76	47.667	41			

Table II. Experimental vapour pressure p_{exp} of 2-propanol and pressure residuals $\Delta p = p_{exp} - p_{cal}$; where p_{cal} has been obtained from Eq. (2).

TABLE III

T/K	p_{exp}/kPa	Δp/Pa	T/K	p_{exp}/kPa	Δp/Pa
323.15	19.530	-76	351.02	53.022	52
331.15	26.530	-58	352.49	55.603	54
333.76	29.220	-41	354.01	58.347	26
336.28	32.051	5	355.20	60.599	32
338.50	34.692	17	356.79	63.699	23
340.34	37.017	33	357.94	65.991	-13
342.37	39.678	3	359.34	68.932	4
344.22	42.282	20	360.52	71.447	-26
346.10	45.068	38	362.10	75.000	4
347.80	47.689	32	363.65	78.538	-48
349.67	50.717	29			

Table III. Experimental vapour pressure p_{exp} of 2,2,4-trimethylpentane and pressure residual $\Delta p = p_{exp} - p_{cal}$; where p_{cal} has been obtained from Eq. (2).

TABLE IV

T/K	p_{exp}/kPa	Δp/Pa	T/K	p_{exp}/kPa	Δp/Pa
275.06	26.653	- 7	303.53	82.991	- 6
275.21	26.800	-39	304.70	86.578	49
276.09	27.880	-25	306.15	91.137	65
277.66	29.926	33	308.34	98.263	-28
279.81	32.789	-12	309.06	100.750	-11
282.08	36.154	36	310.22	104.763	-80
283.82	38.868	27	311.29	108.680	-45
286.14	42.734	6	312.31	112.565	36
288.07	46.231	34	312.73	114.144	18
292.09	54.165	10	313.17	115.797	-22
294.41	59.267	39	313.99	119.029	4
296.80	64.839	- 8	315.15	123.646	34
299.27	71.072	-23			

Table IV. Experimental vapour pressure p_{exp} of n-pentane and pressure residuals $\Delta p = p_{exp} - p_{cal}$; where p_{cal} has been obtained from Eq. (2).

TABLE V

T/K	p_{exp}/kPa	Δp/Pa	T/K	p_{exp}/kPa	Δp/Pa
306.98	26.392	42	323.34	55.906	-21
309.18	29.316	8	324.36	58.418	-31
314.16	37.024	-37	325.33	60.952	16
315.76	39.918	25	326.42	63.872	36
317.07	42.342	- 4	327.29	66.235	2
318.45	45.046	-21	328.24	68.898	-39
319.75	47.737	-27	329.21	71.806	14
320.97	50.392	-25	330.01	74.218	- 2
322.18	53.154	-16	331.32	78.340	- 5

Table V. Experimental vapour pressure p_{exp} of methanol and pressure residuals $\Delta p = p_{exp} - p_{cal}$; where p_{cal} has been obtained from Eq. (2).

TABLE VI

T/K	p_{exp}/kPa	Δp/Pa	T/K	p_{exp}/kPa	Δp/Pa
304.76	11.460	1	334.08	48.816	37
309.86	15.089	12	335.48	51.921	21
313.51	18.215	-20	336.88	55.202	14
316.34	21.054	- 6	338.01	57.978	8
318.54	23.481	-26	339.06	60.670	11
320.70	26.157	14	340.18	63.656	12
323.75	29.576	0	341.13	66.268	- 4
324.96	32.099	11	341.94	68.582	7
326.40	34.352	10	342.81	71.129	-15
328.07	37.186	62	343.88	74.389	-13
329.46	39.594	10	344.90	77.614	- 9
331.15	42.795	35	344.98	77.820	-61
332.67	45.814	16			

Table VI. Experimental vapour pressure p_{exp} of ethanol and pressure residual $\Delta p = p_{exp} - p_{cal}$; where p_{cal} has been obtained from Eq. (2).

TABLE VII

T/K	p_{exp}/kPa	Δp/Pa	T/K	p_{exp}/kPa	Δp/Pa
295.07	26.927	-17	311.50	53.078	17
297.03	29.339	- 4	312.77	55.693	-36
298.87	31.793	40	313.91	58.249	34
301.01	34.734	-25	315.18	61.070	-20
302.83	37.496	1	316.35	63.885	46
304.45	40.078	2	317.43	66.487	22
305.76	42.285	17	318.43	68.969	- 5
307.54	45.414	11	319.52	71.793	- 3
308.78	47.653	-44	322.03	78.598	-51

Table VII. Experimental vapour pressure p_{exp} of acetone and pressure residuals $\Delta p = p_{exp} - p_{cal}$; where p_{cal} has been obtained from Eq. (2).

TABLE VIII

T/K	p_{exp}/kPa	Δp/Pa	T/K	p_{exp}/kPa	Δp/Pa
303.17	15.947	9	328.90	44.759	- 7
306.08	18.101	0	332.64	51.308	101
309.75	21.158	- 8	334.36	54.385	-22
312.92	24.130	-12	335.98	57.559	- 6
315.58	26.892	- 2	337.71	61.136	38
318.33	29.979	-23	339.01	63.833	-32
320.42	32.548	- 5	340.79	67.750	-63
322.72	35.566	5	341.93	70.450	8
324.33	37.786	-11	344.88	77.607	-15

Table VIII. Experimental vapour pressure p_{exp} of benzene and pressure residuals $\Delta p = p_{exp} - p_{cal}$; where p_{cal} has been obtained from Eq. (2).

TABLE IX

SUBSTANCE	A	B	C
acetone	6.384897	1288.8889	-34.9215
benzene	6.048137	1222.364	-50.9121
2 - propanol	7.435340	1677.407	-46.4170
methanol	7.211740	1583.890	-33.4690
2,2,4 - trimethylpentane	6.146780	1386.248	-37.5840
n-pentane	6.206773	1183.321	-27.5503
ethanol	6.404289	1690.380	-38.3550

Table IX. Constants of the Antoine equation.

TABLE X

SUBSTANCE	T_b/K		(dp/dt)/kPa K^{-1}	
	(a)	Ref. 1	(b)	Ref. 1
acetone	329.24	329.28	3.472	3.463
benzene	353.30	353.25	3.119	3.122
2 - propanol	355.35	355.48	4.101	4.102
methanol	337.71	337.66	3.992	3.992
2,2,4 - trimethylpentane	372.34	372.39	2.886	2.886
n - pentane	309.22	309.22	3.480	3.458
ethanol	351.47	351.48	4.023	4.003

Table X. Comparison of calculated and literature values of normal boiling point and the first differential coefficient.

[a] values from the Antoine equation at p = 101.325 kPa.

[b] values from the Antoine equation at the normal boiling point.

TABLE XI

	ΔH/kJ mol^{-1} at 298.2 K		ΔH/Kj mol^{-1} at T_b		(% error)[d]	
					298.2 K	T_b
acetone	31.0	31.84(17)	26.9	30.44(17)	2.70	-2.84
benzene	33.8	33.47(18)	31.1	31.06(18)	-0.98	0.13
2-propanol	44.7	44.98(19)	40.7	39.83(19)	0.63	2.14
methanol	37.9	37.96(18)	35.9	35.92(18)	0.16	-0.06
2,2,4-trimethyl-pentane	35.1	35.52(18)	30.4	31.12(18)	1.20	-2.40
n-pentane	26.8	26.44(18)	26.4	25.84(18)	-1.34	-2.12
ethanol	42.2	41.84(17)	39.1	39.42(17)	-0.85	0.82

Table XI. Comparison of calculated and literature values of the molar heat of vaporization at 298.2° K and at the normal boiling point.

[d] $$(\%\ \text{error}) = \frac{\Delta H_{lit} - \Delta H_{cal}}{\Delta H_{cal}} \cdot 100$$

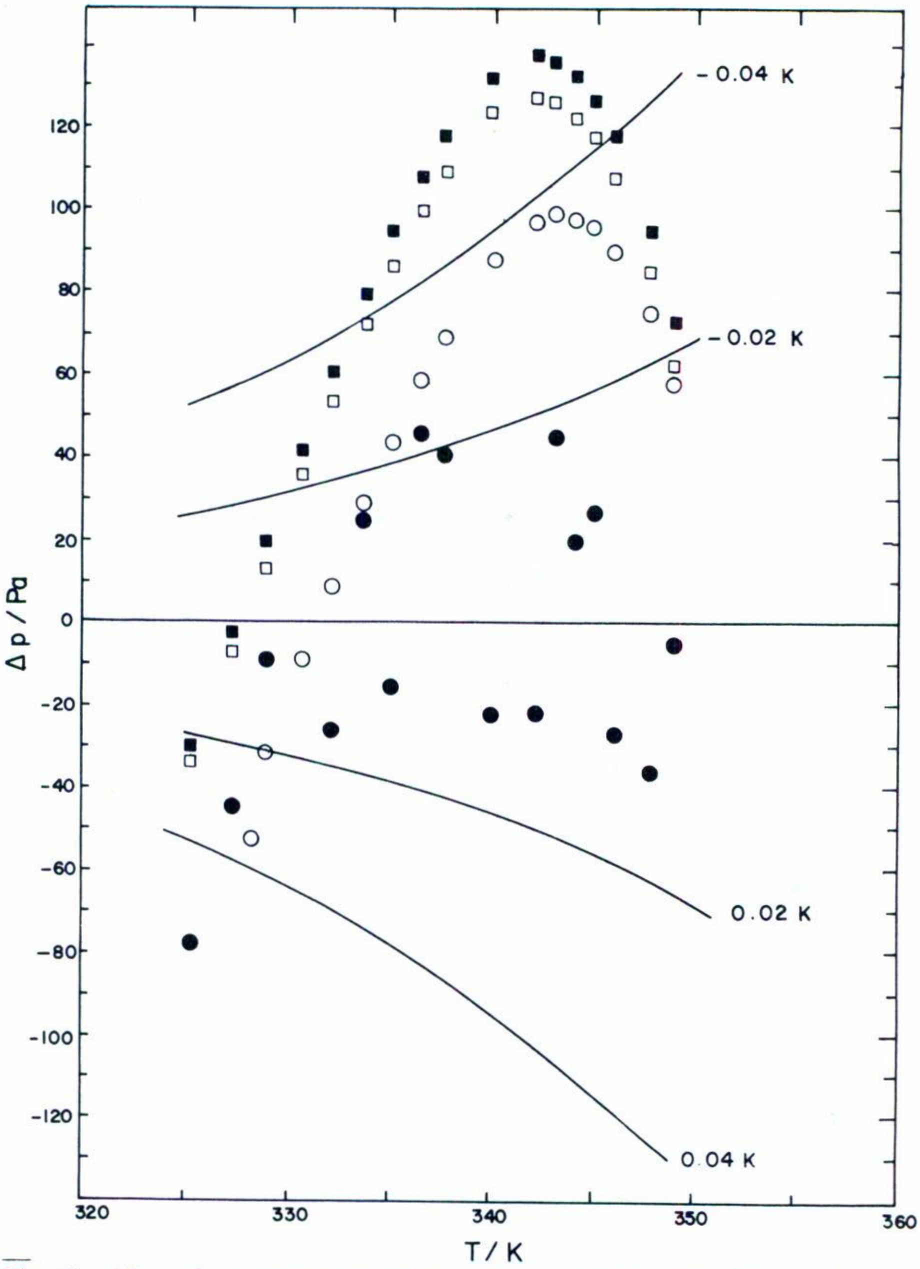

Fig. 2. Plot of pressure residuals Δp for 2-propanol from Eq. (2) for values of this work and values reported by other authors. The curved lines correspond to Δp values for the stated ΔT values of temperature, i.e., $\Delta p = -(dp/dT)\ \Delta T$. This work ●, Hirata[12] ○, Ambrose[13] □, Ohe[14] ■.

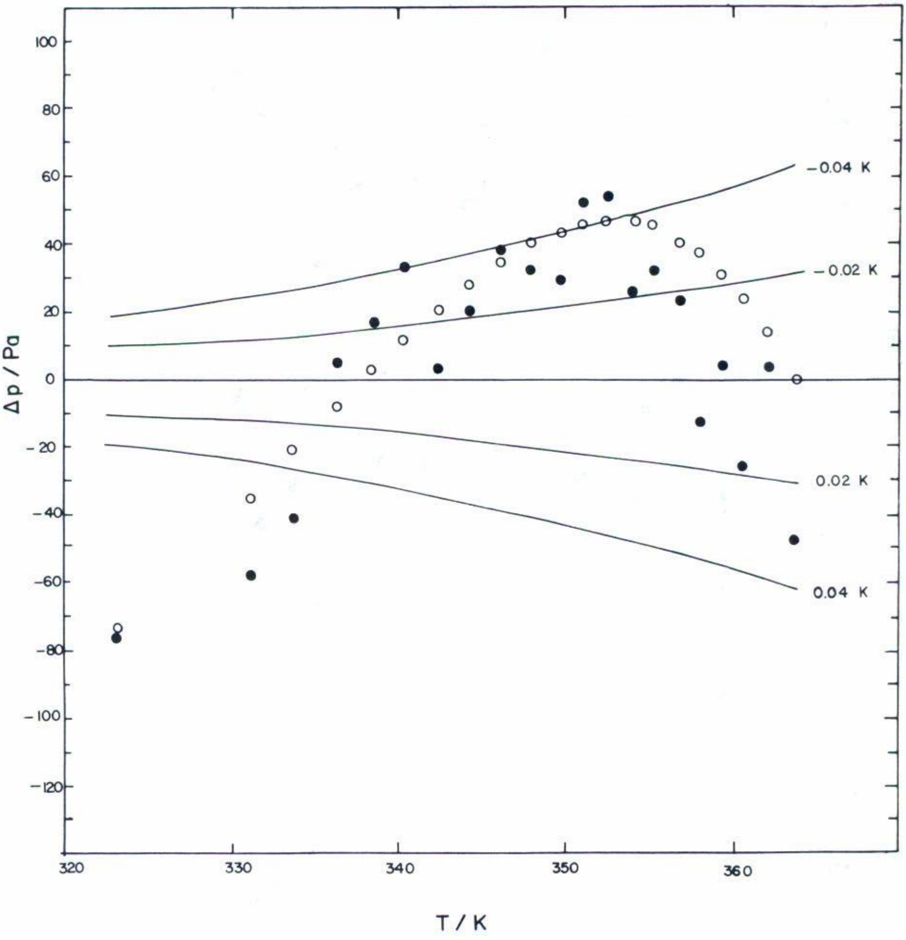

Fig. 3. Plot of pressure residuals Δp for 2,2,4-trimethylpentane from Eq. (2) for values of this work and values reported by other authors. The curved lines correspond to Δp values for the stated ΔT values of temperature, i.e. $\Delta p = -(dp/dT)\,\Delta T$. This work ●, Hirata[12] ○.

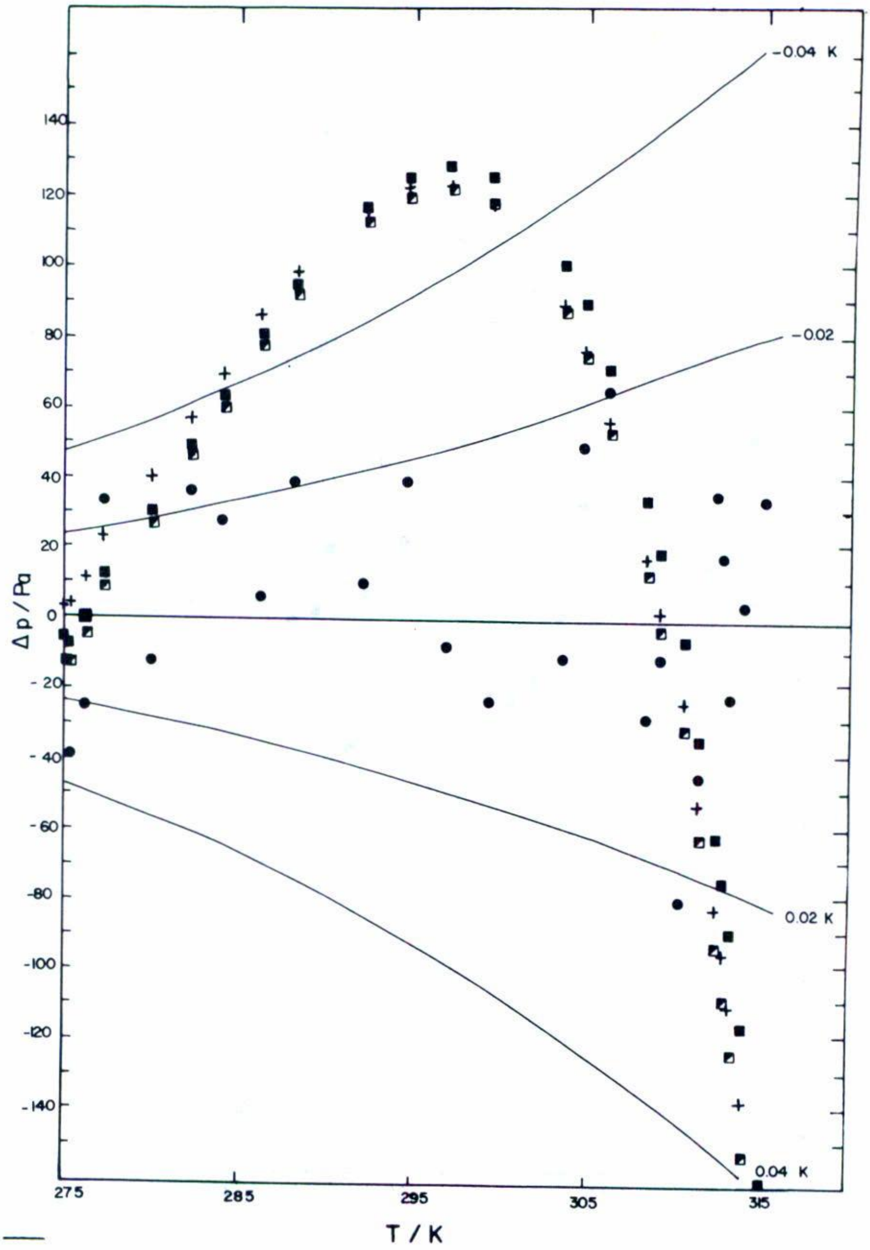

Fig. 4. Plot of pressure residuals Δp for n-pentane from Eq. (2) for values of this work and values reported by other authors. The curved lines correspond to Δp values for the stated ΔT values of temperature, i.e. $\Delta p = -(dp/dT)\,\Delta T$. This work ●, A.P.I.[1] ◪, Willingham[10] +, Ohe[14] ■.

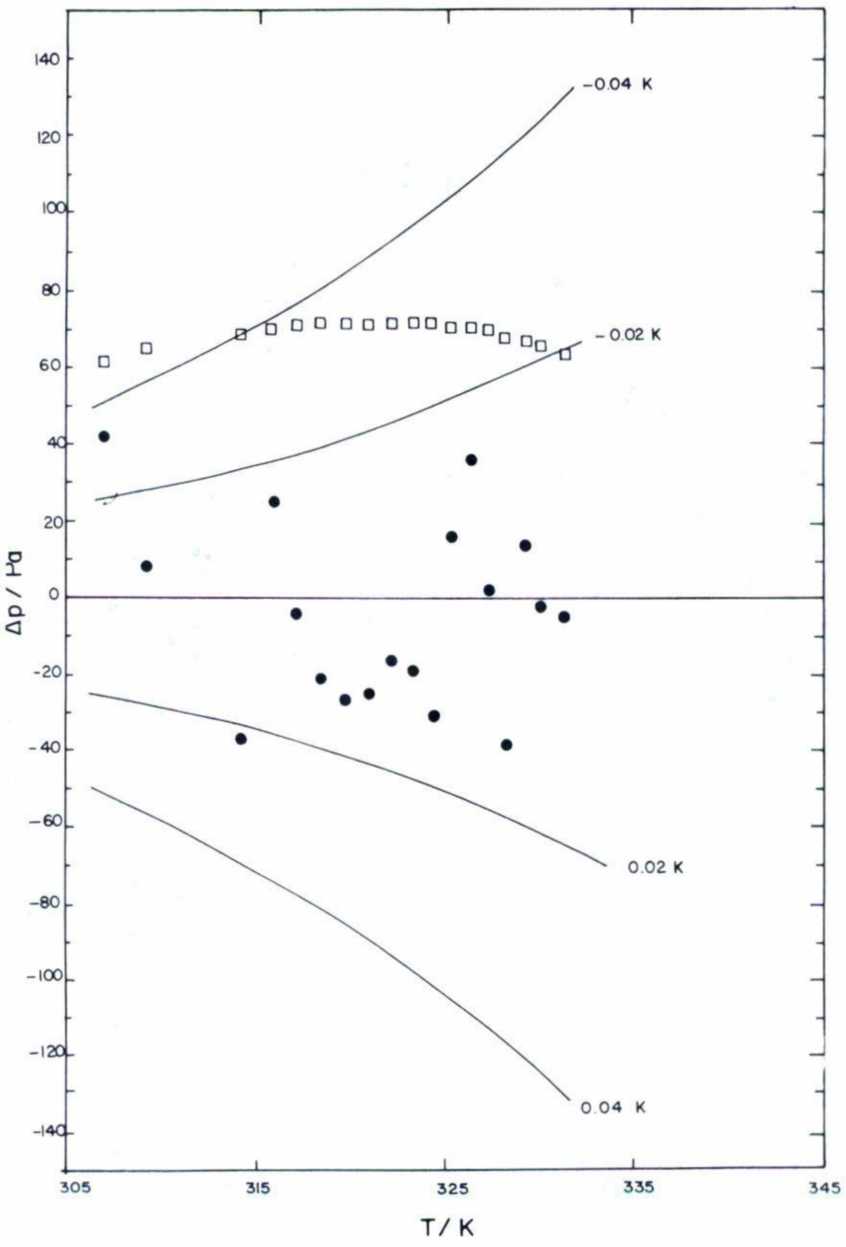

Fig. 5. Plot of pressure residuals Δp for methanol from Eq. (2) for values of this work and values reported by other authors. The curved lines correspond to Δp values for the stated ΔT values of temperature, i.e. $\Delta p = -(dp/dT)\,\Delta T$. This work ●, Ambrose[13]□.

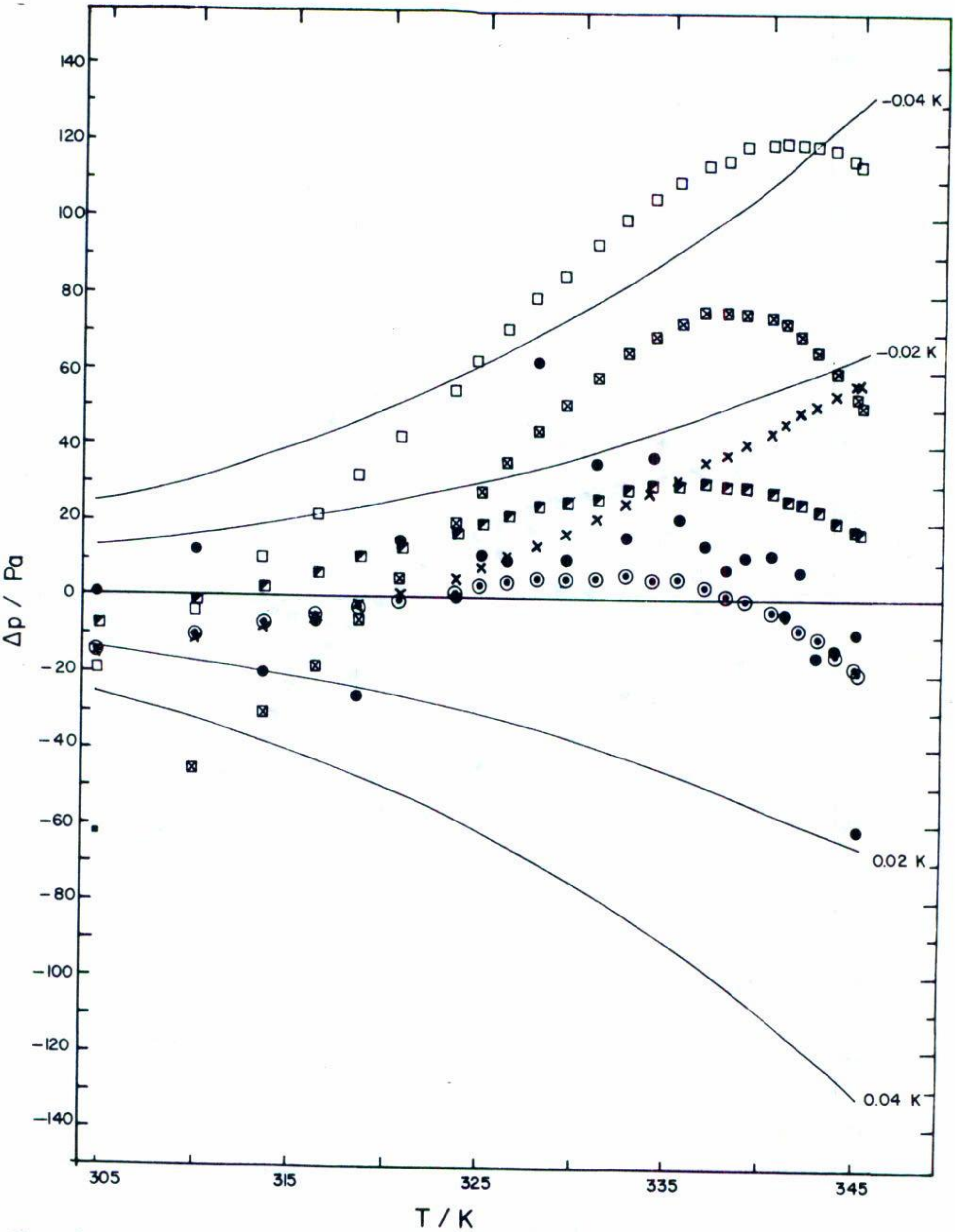

Fig. 6. Plot of pressure residuals Δp for ethanol from Eq. (2) for values of this work and values reported by other authors. The curved lines correspond to Δp values for the stated ΔT values of temperature, i.e. $\Delta p = -(dp/dT)\,\Delta T$. This work ●, Ambrose[13] □, A.P.I.[1] ◪, Reid[9] ⊙, Kretschmer[15] X, Holmes[16] ⊠.

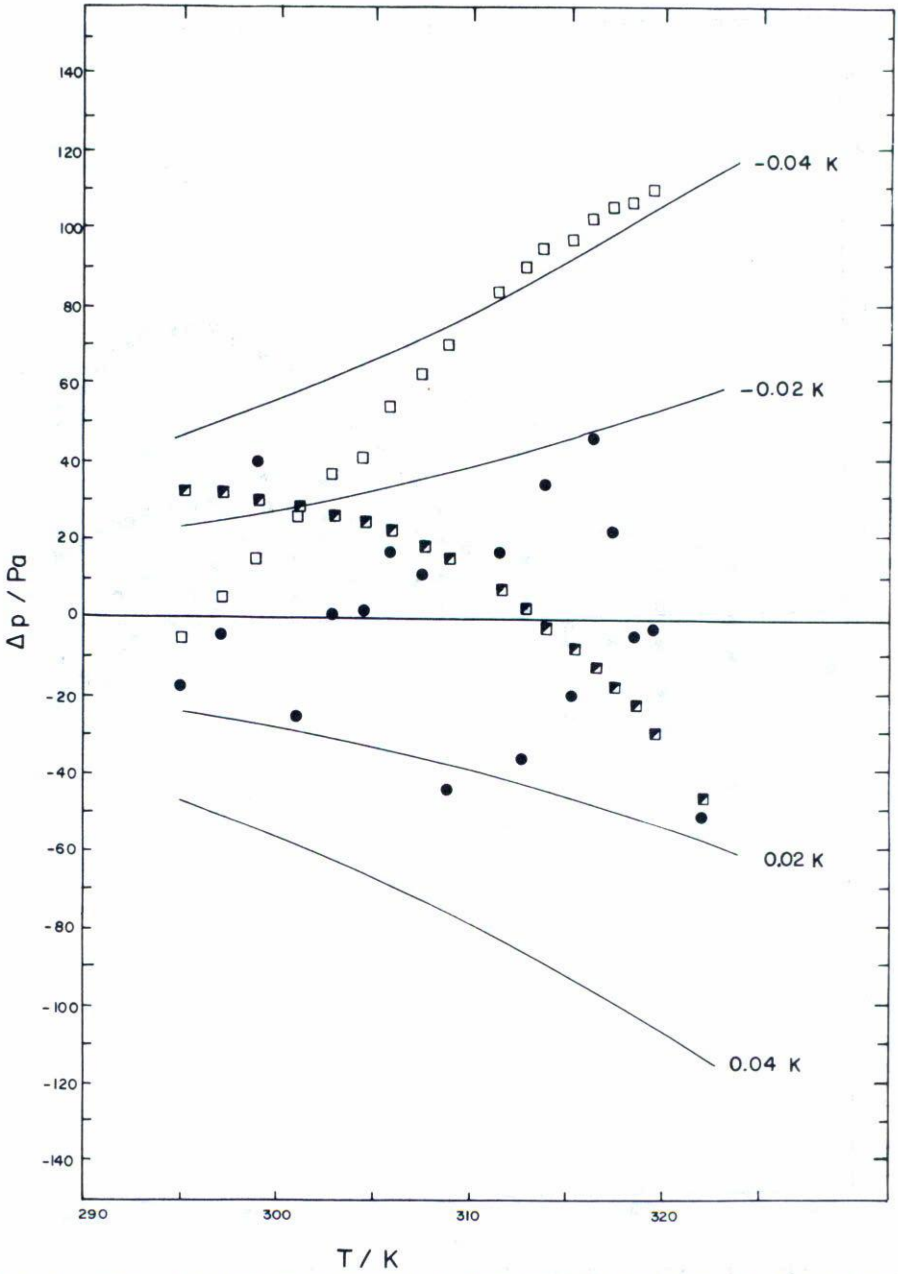

Fig. 7. Plot of pressure residuals Δp for acetone from Eq. (2) for values of this work and values reported by other authors. The curved lines correspond to Δp values for the stated ΔT values of temperature, i.e. $\Delta p = -(dp/dT)\,\Delta T$. This work ●, Ambrose[8] □, A.P.I.[1] ◩.

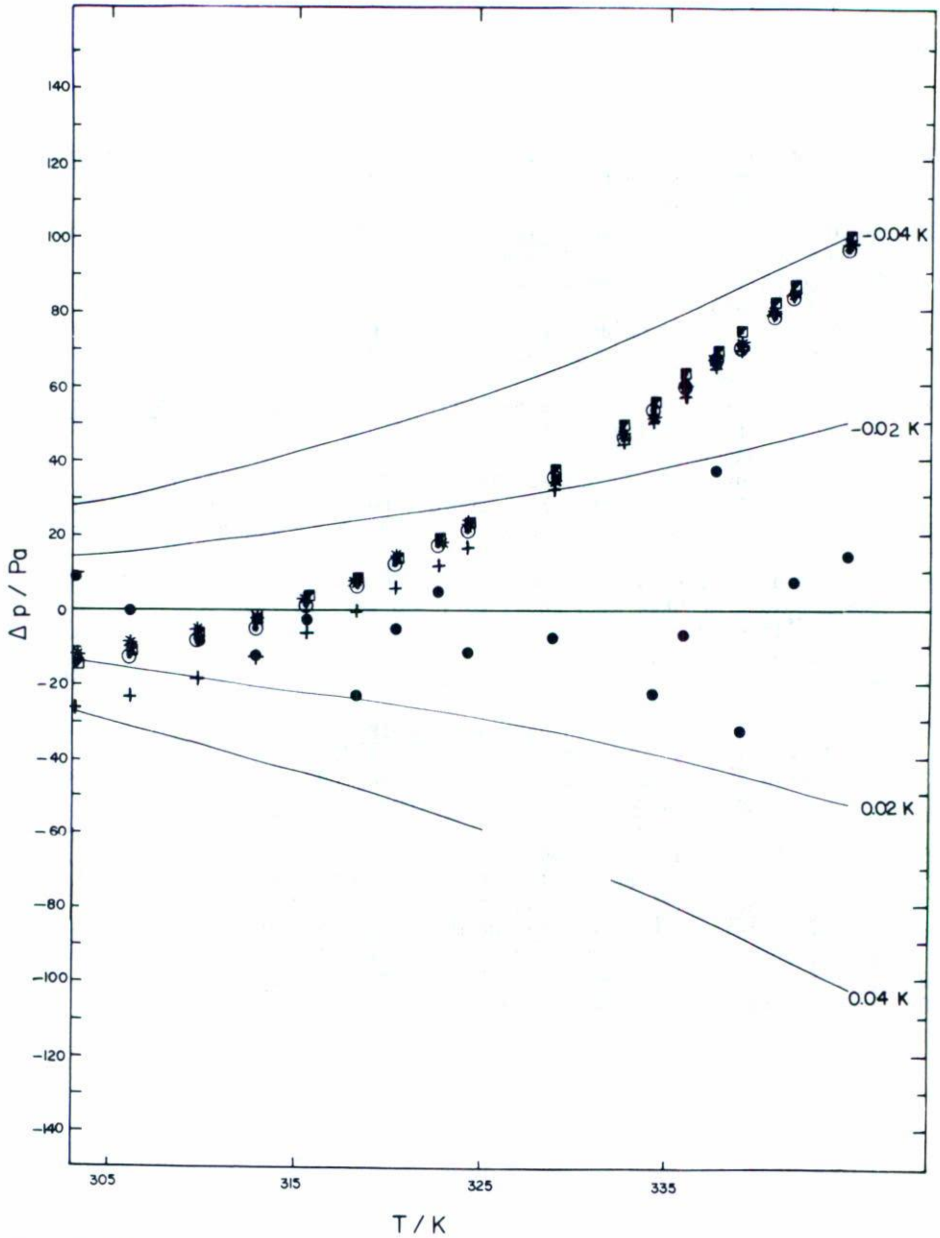

Fig. 8 Plot of pressure residuals Δp for benzene from Eq. (2) for values of this work and values reported by other authors. The curved lines correspond to Δp values for the stated ΔT values of temperature, i.e. $\Delta p = -(dp/dT)\ \Delta T$. This work ●, A.P.I.[1] ◪, Reid[9] ⊙, Willingham[10] +, Forziatti[11] ⋆.

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