the superior base line stability at low temperatures (see Experimental section), the results between 300 and 400K are of significantly higher accuracy, probably ± 0.05 cal K⁻¹ g atom⁻¹. All the results were fitted to polynomials of successively higher degree, and the fit to a first degree polynomial (C₁ + C₂ T) gave a residual mean square ($N^{-1} \Sigma [C_p(\text{calcd}) - C_p(\text{exptl})]^2$) of the same order as the RMS corresponding to the estimated accuracy (± 0.1 cal K⁻¹ g atom⁻¹) of the results. This polynomial, $C_p(\text{GaAs}) = (5.35 \pm 1.16 \times 10^{-3} \text{ T})$ cal K⁻¹ g atom⁻¹, was used to calculate the smoothed results in Table I.

The smoothed results are compared in Figure 1 with the corresponding smoothed data of Cox and Pool (7) (298-1250K) and Lichter and Sommelet (3) (298-1513K, the melting temperature). Our results are systematically higher than those of Cox and Pool (given by $C_p = 5.4 + 7.3 \times 10^{-4} T$) and are in closer agreement with those of Lichter and Sommelet [Lichter and Sommelet's smoothed C_p results at 600 and 1300K are not linear with the other smoothed C_p results in their Table 3. Further, these smoothed results (given by $C_p/\text{cal K}^{-1}$ g atom⁻¹ = 5.23 + 0.0014 *T*, except for those results at 600 and 1300K) are not in agreement with an analytical expression, given in the form $C_p = 3 R(a' + b'T) = 5.66 + 8.34_5 \times 10^{-4} T$, contained in their. Table 5], although our results display a significantly larger temperature coefficient. Confidence in our results is increased by the continuity of our values in the range 300–400K with the low temperature (10–273K) heat capacities of Piesbergen (4) (see inset to Figure 1).

Acknowledgment

We thank E. Gosling for the helpful discussions.

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Vapor-Pressure Relations for 15 Hydrocarbons

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Experimental values of vapor pressure for 15 hydrocarbons are measured in the low-pressure range 0.1–25 mm Hg by means of the inclined-piston deadweight gage and in the range 71–2025 mm Hg by means of comparative ebulliometers. Correlations of the present results with selected literature values are given in terms of Cox equations.

. Vapor pressure-temperature relations of liquid and solid phases are a requisite for comprehensive thermodynamic studies. The presently reported experimental vapor pressures and derived parameters of Cox's (4) vaporpressure equations for 15 hydrocarbons are part of a larger project carried out by the Bureau of Mines Bartlesville (Okla.) Energy Research Center to determine the thermodynamic properties of hydrocarbons in or related to petroleum. Except for the vapor-pressure values of Willingham et al. (18), Forziati et al. (7), and Pitzer and Scott (14), which in some cases are correlated with present results, there are no experimental data of comparable quality for these compounds in the literature.

Materials

The samples were American Petroleum Institute (API) research-grade hydrocarbons, purified and made available by the API Research Project 58 at Carnegie-Mellon University, A. J. Streiff, Director. The purity of most of the compounds was determined from freezing temperatures vs. fraction melted data observed as a purity monitor by Project 58 or during low-temperature calorimetric measurements made in this laboratory under API Project 62. (Details of the freezing-point measurements carried out on individual compounds in connection with low-temperature thermal studies will appear in separate reports from this laboratory.) An additional check on the purity of seven of the samples was furnished by simultaneous observations of the boiling and condensing temperatures. The small observed differences in temperature (Table I, column 1) substantiate the calorimetric purity values for these compounds and suggest that the impurities present did not affect significantly the observed boiling points of the samples.

Experimental Methods

Static measurements. An inclined-piston manometer, described by Douslin and McCullough (5) and Douslin and Osborn (6), was used for low-pressure measurements below and slightly above room temperature. Briefly, the method consisted of balancing the known weight, W, of a free piston declined from the horizontal by a measured angle, θ , against the pressure exerted by the vapor of the sample placed in a thermostated bath. From the measured area and weight of the piston, the angle of declination, and the acceleration of gravity, the vapor pressure was calculated as a primary quantity, $p = (g/g_{std})(W \sin \theta)/A$. Corrections were applied, when significant, for vapor head between the piston face and the surface of the liquid.

Ebulliometric measurements. The comparative ebulliometric method described by Waddington et al. (17), and more recently by Osborn and Douslin (12), was used on seven of the hydrocarbons over a pressure range from 70 to 2025 mm Hg. Briefly, the ebulliometric method consisted of comparing boiling temperatures of the hydrocarbon with the boiling temperatures of standard water or standard benzene under equal pressure of a helium gas blanket. From the boiling temperature of the standard substance, the pressure in the ebulliometers was determined by reference to the International Steam

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Table I. Constants of Cox Vapor-Pressure Equation

	Δt,ª K	Impurity, mol %	Constants of Cox equation				Range,	
Compound			Φ	PΦ	a	Ь	c	K
n-Pentane	0.001	0.026	309.218	760	0.813570	-7.73685×10^{-4}	$+9.06731 \times 10^{-7}$	268-342
Neopentane	0.001	0.05	282.650	760	0.802264	-8.70026×10^{-4}	$+11.22918 \times 10^{-7}$	268-314
Bicyclo[2.2.1]heptane		0.07	247.109	0.942	0.101139	$+8.01159 imes 10^{-3}$	$-1.91740 imes 10^{-5}$	217–248
2,3-Dimethylpentane		0.20°	362.932	760	0.836568	$-7.45853 imes 10^{-4}$	$+7.52716 \times 10^{-7}$	208–364
1,4-Dimethylbenzene (solid)		0.004	286.374	4.354	-0.303858	$+9.78538 \times 10^{-3}$	$-1.77986 imes 10^{-5}$	247-t.p.ª
1,4-Dimethylbenzene (liquid)	0.001	0.004	286.374	4.354	1.004831	$-5.00738 imes 10^{-4}$	$+4.06552 \times 10^{-7}$	t.p453ª
1-Methyl-1-ethylcyclopentane	0.001	0.031	394.681	760	0.843416	$-7.17938 imes 10^{-4}$	$+6.77358 \times 10^{-7}$	238-436
1-Methyl-cis-2-ethylcyclopentane		0.0570	401.209	760	0.857007	$-7.70496 imes 10^{-4}$	$+7.62177 \times 10^{-7}$	238-403
2-Methylheptane		0.031	390.804	760	0.877373	$-8.25991 imes 10^{-4}$	$+8.03484 \times 10^{-7}$	233-392
3-Methylheptane		0.027	392.078	760	0.873873	$-8.03154 imes 10^{-4}$	$+7.67368 \times 10^{-7}$	238-393
2,3,4-Trimethylpentane	0.001	0.05°	386.622	760	0.842584	-7.24076×10^{-4}	$+6.94048 \times 10^{-7}$	222-427
1-Methyl-cis-3-ethylcyclohexane	0.001	0.01°	421.616	760	0.850755	$-6.76973 imes 10^{-4}$	$+5.94159 imes 10^{-7}$	348-465
2,2,3-Trimethylhexane		0.25°	303.148	15.040	0.969466	-5.01211×10^{-4}	$+3.68675 \times 10^{-7}$	238-304
2,2,4-Trimethylhexane	·	0.25°	303.150	20.712	0.998704	$-8.26595 imes 10^{-4}$	$+9.40240 \times 10^{-7}$	238-304
2,2,5-Trimethylhexane		0.14°	397.243	760	0.877846	$-8.47083 imes 10^{-4}$	$+8.23570 \times 10^{-7}$	238-399
2-Methyldecane	0.001	0.021	462.368	760	0.944802	$-8.89968 imes 10^{-4}$	$+7.59345 imes 10^{-7}$	273–463

^a Ebuilition minus condensation temperature at 760 mm Hg. ^b Glc analysis, Bureau of Mines. ^c API research-grade reported impurity. ^d t.p. = triple-point 286.374K.

Tables (10, 13), the Stimson-Cragoe correction (16) for the vapor pressure of water, and the API Research Project 44 Tables (15) for the vapor pressure of benzene (Table A-III, Appendix).

For both static and ebulliometric measurements, temperatures were measured with a precision of 0.001° on the International Temperature Scale [T, K = t, °C (Int., '68) + 273.15] (9) by use of 25-ohm platinum resistance thermometers that had been calibrated by the National Bureau of Standards and checked at the triple-point temperature of a certified benzoic acid cell. Periodic observations of the ice-point resistances of the thermometers showed no significant change. The resistances of the thermometers were measured to a precision of 2×10^{-5} ohm with a high-sensitivity galvanometer and Mueller G-2 bridge, the coils of which had been compared and adjusted to a standard resistor calibrated at the National Bureau of Standards.

Results

The presently observed values of vapor pressure obtained by inclined-piston and ebulliometric methods (Table II) and selected vapor-pressure values from the literature were correlated by the Cox (4) equation, log_{10} $p/p_{\Phi} = A(1 - \Phi/T)$, where $\log_{10} A = a + bT + cT^2$, and the constants a, b, c, and Φ (Table I) were derived from a least-mean-square treatment of the data. The experimental points were weighted according to the factors, $W_i = [(p_i/p_{\Phi}) \ln (p_i/p_{\Phi})]^2/\sigma_i^2$, in which $\sigma_i^2 = [\sigma_p^2 + \sigma_i^2]^2$ $(dp/dt)^2 \sigma_T^2$] was the calculated experimental uncertainty for the ith point according to the experimentally based uncertainties, σ_p in pressure and σ_T in temperature. The constant Φ was iterated as part of the least-mean-square analysis until the best fit of the experimental points was obtained. Because solid and liquid regions were studied for 1,4-dimethylbenzene, ho_{Φ} and Φ were assigned values at the triple-point pressure and temperature, 4.354 mm of Hg and 286.374K, respectively. In this case, the assigned value of Φ was not iterated as part of the leastmean-square evaluation of the Cox parameters.

Display of pressure deviations from Cox equations over a large temperature range accented the high-temperature, high-pressure end when a single pressure or temperature ordinate was used. When the ratio $\Delta p/\sigma$ was displayed, the appreciation for absolute magnitudes of

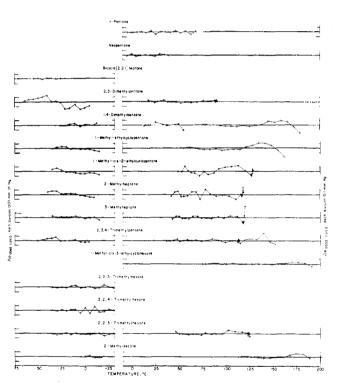


Figure 1. Deviations of experimental points from Cox equations. Δ , present results inclined-piston manometer; O, present results ebulliometric; Δ , Pitzer and Scott (14); \bullet , Forziati et al. (7) and Willingham et al. (18)

 Δp was lost because the numerical values for σ were not obvious. As a compromise, a pressure deviation plot was given for two temperature ranges (Figure 1), each range having a separately scaled ordinate chosen to produce percentage deviations of comparable orders of magnitude.

n-Pentane. The present measurements (Table II) intersect the upper range covered by Messerly and Kennedy (11), -65° to $+25^{\circ}$ C, and overlap the entire range of Willingham et al. (18), $+13^{\circ}$ to $+37^{\circ}$ C, with which they are in excellent agreement. The extended Cox equation (Table I) obtained from the present results is in fair agreement with the lower range of measurements re-

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0.642 70.881 81.701 70.453	133.04 IU.UUU	8./U8 1-Meti	I-Methyl-cis-3-ethyl-	-30.000 0.358	146.817	233.85
	149.51	, cr	cyclohexane	25.000 0.553	153.752	289.26
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82.897	233.85	75.156	56 71.929	-15.000 1.226	167.780	433.67
118.15 89.198	289.26	78.346	46 81.701		174.872	525.95
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149.51 101.967	433.67	84.766			189.220	760.00
433	525.95	87.995				
955	634.05	91.238				
121.529 /60	/60.00	94.498	98 149.51			
				20.000 12.068		
* 1 mm Hc 0 1332201 LN / 2				25.000 15.899		

ported by Beattie et al. which extend from 100° to the critical temperature (3). The agreement with Messerly and Kennedy is good below $+4^{\circ}$ but poor from $+10^{\circ}$ to +25°C.

Neopentane. Although neopentane is not uncommon commercially and its structure has presented a special case for statistical-mechanical calculation, good vaporpressure data were not available over much of the present range of measurement. Aston and Messerly's (2) experimental pressures in the range -15° to $+10^{\circ}$ C are from 0.2 to 1.5 mm of Hg higher than present values. This difference is less than the product of dp/dt and their assumed error of temperature measurement. Howard et al. (8) report a single boiling temperature 9.499°C (IPTS-1968 at 760 mm of Hg) that is in excellent agreement with the present value, 9.500°C. Vapor-pressure values based on the Antoine equation that appears in API 44 (1953) tables (15) seldom deviate from present experimental values by more than 0.2 mm of Hg.

Bicyclo[2.2.1]heptane (Norbornylane). Measurements were carried out from -55° to -26° C on equilibrium crystals II delineated as the stable crystalline phase during calorimetric studies (From measurements carried out in the low-temperature laboratory of the Bartlesville Energy Research Center, Bureau of Mines, crystals II were stable from -141.65° to $+32.75^{\circ}$ C). Above -26° C the vapor-pressure sample was unstable, contrary to expectations. Literature values are not available for comparison with present results.

2.3-Dimethylpentane. 1-methyl-cis-2-ethylcyclopentane, 2-methylheptane, 3-methylheptane, 2,3,4-trimethylpentane, and 2,2,5-trimethylhexane. The compounds in this group were measured at relatively low pressures with the inclined-piston manometer (5, 6). Data for higher pressures were taken from refs. 7 and 18. Although none of the data sets overlapped, each was easily fitted with a common Cox equation (Table 1) with deviations generally less than 0.1% at low pressure and less than 0.02% at high pressure.

1-Methyl-1-ethylcyclopentane, 1-methyl-cis-3-ethylcyclohexane, and 2-methyldecane. The compounds in this group were measured in the low-pressure range with the inclined-piston manometer (5, 6) and in the high-pressure range by comparative ebulliometry (12, 17). The temperature ranges were separated by 37° for 1-methyl-1-ethylcyclopentane and by 92° for 2-methyldecane. No data in the low-pressure range were obtained for 1methyl-cis-3-ethylcyclohexane. The data for each compound were correlated with a single Cox equation (Table 1) with deviations less than 0.1% at low pressures and 0.01% at the highest pressure.

2,2,3-Trimethylhexane and 2,2,4-trimethylhexane. The measurements were confined to the low-pressure range of the inclined-piston manometer. Cox equations (Table 1) deviate from the measured values by generally less than 0.1%

1,4-Dimethylbenzene. The complete investigation covered more than four orders of magnitude in pressure for solid and liquid states and yielded a derived value for the triple-point pressure, 4.354 mm of Hg, at the calorimetrically determined triple-point temperature, 13.224°C. The point of intersection of the solid and liquid vapor-pressure curves furnishes common temperature and pressure parameters in the Cox equations (Table 1). Pitzer and Scott (14) reported vapor pressures from 25° to 60°C which are in good agreement with the present results.

Conclusions

Values of dp/dt and R in p derived from the experimental vapor-pressure measurements are accurate

enough for most thermodynamic studies in which the enthalpy and entropy of equilibrium phase change are needed to convert experimental thermodynamic properties to gas-phase values.

Appendix

Table A-III

Water reference substance ⁴		Benzene reference substance		
Boiling temp, °C	Press, mm Hg	Boiling temp, °C	Press, mm Hg	
60	149.51	19.071	71.929	
65	187.69	21.728	81.701	
70	233.85	24.396	92.592	
75	280.26	27.075	104.71	
80	355.34	29.765	118.15	
85	433.67	32.467	133.04	
90	525.95	35.179	149.51	
95	634.05			
100	760.00			
105	906.02			
110	1074.43			
115	1267.75			
120	1488.78			
125	1740.27			
130	2025.33			

^a The table for water was prepared from ref. 9 by conversion to the even values of temperature on the 1968 International Practical Temperature Scale. The values are close to those given by Ambrose and Lawrenson (1).

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The authors gratefully acknowledge the assistance of Bureau of Mines staff members, B. E. Gammon for the original computer program of the least-mean-square derivation of the Cox equation constants, R. T. Moore for his assistance with some of the calculations, and P. H. Clopp for technical assistance with the apparatus.

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