(4) Rastogi, R. P.; Singh, N. B.; Dwivedi, K. D. *Ber. Bunsen-Ges. Phys. Chem.* **1981**, *85*, 85.
(5) Singh, N. B.; Dwivedi, K. D. *J. Sci. Ind. Res.* **1982**, *41*, 98.
(6) Rastogi, R. P.; Rastogi, V. K. *J. Cryst. Growth* **1969**, *5*, 345.
(7) Dean, J. A.; Lange, N. A. *Lange's Handbook of Chemistry* 13th ed.; Mcgraw-Hill: New York, 1985; Section 7.
(8) Rastogi, R. P.; Bassi, P. S. *J. Phys. Chem.* **1964**, *68*, 2398.
(9) Rastogi, R. P.; Chatterji, A. C. *J. Phys. Chem.* **1955**, *59*, 1.
(10) Richards, J. H.; Walker, S. *Trans. Faraday Soc.* **1961**, *57*, 406.

Received for review May 17, 1988. Accepted November 1, 1988.

---

# Vapor Pressure of *n*-Alkanes Revisited. New High-Precision Vapor Pressure Data on *n*-Decane, *n*-Eicosane, and *n*-Octacosane†

**Robert D. Chirico, An Nguyen, William V. Steele,* and M. Michael Strube**
*IIT Research Institute, National Institute for Petroleum and Energy Research, P.O. Box 2128, Bartlesville, Oklahoma 74005*

**Costa Tsonopoulos***
*Exxon Research and Engineering Co., Florham Park, New Jersey 07932*

**New vapor pressure measurements on *n*-decane (268–490 K), *n*-eicosane (388–626 K), and *n*-octacosane (453–575 K) have been made with a modified ebulliometer and an inclined piston gauge. Benzene and water were the standards in the ebulliometric measurements on *n*-decane and *n*-eicosane, while *n*-decane was the standard for the measurements on *n*-octacosane. The high-quality data for *n*-decane, which were confirmed by a "third-law" analysis, suggest that reported literature data are in error. Similar concerns are raised about reported *n*-eicosane data. The vapor pressure data were regressed with the Cox equation, using as reference the normal boiling point.**

## Introduction

The thermodynamic and thermophysical properties of high molecular weight organic compounds are of increasing importance in the utilization of fossil fuels. The continued fall in demand for residual fuels, the rise in the specific gravity of petroleum crudes, and the eventual shift to fuels derived from oil shale, tar sands, and the liquefaction of coal all contribute to this increasing importance. Information on high molecular weight organic compounds will form the basis for characterization of both heavy petroleum and synthetic liquids.

In the areas of thermophysical property measurement and correlation, the most extensively studied group of organic compounds is the normal alkanes. Because of the availability of extensive experimental information for *n*-alkanes, most property correlations are initially tested using those data. However, tables of thermodynamic and thermophysical properties of *n*-alkanes (or any other class of compounds) often contain values derived by correlation. For example, the TRC tables (*1*) contain vapor pressure values for the *n*-alkanes methane through hectane ($C_{100}$); however, the reported values for $C_{21}$ through $C_{100}$ were obtained from the correlation derived by Kudchadker and Zwolinski (*2*).

In this paper we report new experimental vapor pressures for *n*-decane, *n*-eicosane, and *n*-octacosane. The *n*-decane data were obtained to confirm those of Willingham et al. (*3*), test the low-pressure data of Carruth and Kobayashi (*4*), which have been questioned by Scott and Osborn (*5*), and establish *n*-decane as a secondary standard for ebulliometric vapor pressure measurements. Data for *n*-eicosane and *n*-octacosane are presented as representative examples of high molecular weight compounds whose vapor pressures can be measured with high precision in our laboratory. Measurements on both compounds illustrate the range of our present apparatus. The results are compared with literature data [API 42 (*6*), Macknick and Prausnitz (*7*), and Myers and Fenske (*8*)] and the correlation used in the derivation of the values reported in the current TRC tables (*1*, *2*).

## Experimental Section

***Materials.*** All three *n*-alkane samples were obtained from commercial sources and subjected to stringent purification by Professor E. J. Eisenbraun's group at Oklahoma State University. Gas–liquid chromatographic (GLC) analyses performed on the *n*-alkane samples prior to the experimental measurements confirmed their high purities: *n*-decane had less than 0.002% impurities, *n*-eicosane had 0.05% impurities, and *n*-octacosane had 0.016% impurities.

The water, used as a reference material in the ebulliometric vapor pressure measurements, was deionized and distilled over potassium permanganate. The benzene, used as the other reference material for the ebulliometric measurements, was obtained from the American Petroleum Institute (API) as Standard Reference Material No. 210X-5s. Prior to its use, it was dried by vacuum transfer through Linde 3A molecular sieves.

***Physical Constants and Standards.*** Molar values are reported in terms of the Atomic Weights of 1969 (*9*, *10*), and the gas constant, $R = 8.31441\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, adopted by CODATA (*11*). The platinum resistance thermometers used in these measurements were calibrated with a thermometer previously standardized at the National Bureau of Standards. All temperatures are in terms of the International Practical Temperature Scale of 1968, IPTS-1968 (*12*). Measurements of mass, time, electrical resistance, and potential difference were made in terms of standards traceable to calibrations at the National Bureau of Standards.

***Apparatus and Procedures. Ebulliometric Vapor Pressure Measurements.*** The essential features of the ebulliometric equipment and procedures are extensively described in the literature (*13*, *14*). The ebulliometers were used to reflux the substance under study with a standard of known vapor pressure

---

† Contribution No. 288 from the Thermodynamics Research Laboratory at the National Institute for Petroleum and Energy Research.
* To whom correspondence should be addressed.

under a common helium atmosphere. The boiling and condensation temperatures of the two substances were determined, and the vapor pressure was derived by using the condensation temperature of the standard, water, benzene, or *n*-decane.

The standard vapor pressures of water used were those tabulated by Osborne et al. (*15*) in conjunction with the Stimson–Cragoe correction (*16*) and conversion to IPTS-1968 (*12*). Over the years, this laboratory has reassessed the standard vapor pressure of benzene three times (*14*, *17*, *18*). Because this has caused some confusion, we give here a definitive determination of the set point values.

The available literature data (corrected to IPTS-1968) on the vapor pressure of benzene were assessed for accuracy and precision. The "best" available data were assessed to be those given by Scott and Osborn (*5*) and Forziati et al. (*19*). The benzene vapor pressure data reported by Willingham et al. (*3*) show a systematic deviation relative to those given by both Scott and Osborn (*5*), and Forziati et al. (*19*). The Cox equation was fitted to the vapor pressure data of Scott and Osborn (*5*) and Forziati et al. (*19*) (using the methodology described under Vapor Pressure Fits to the Cox Equation), and the pressures at the set benzene temperatures were calculated with the derived constants. The derived values are listed in Table VI.

As a check on the validity of the vapor pressure data and the derived Cox coefficients, the enthalpy of vaporization of benzene was calculated according to the Clapeyron equation (see Enthalpies of Vaporization) and were compared with values determined by vapor flow calorimetry (*20*). In the calculations, second virial coefficients from Todd et al. (*20*) and literature densities (*1*) were used in the calculation of $\Delta_l^g V_m$ (the difference between molar liquid and gas volumes). The maximum deviation between the calculated and measured enthalpies of vaporization was 37 $J \cdot mol^{-1}$ (at 298.09 K). This deviation is well within the uncertainty interval in the calculated value, i.e., 50 $J \cdot mol^{-1}$.

Modifications have been made to the previously described equipment (*14*) to permit operation to near 700 K and automated data acquisition. The sample ebulliometer was enclosed in an insulated box similar to the one used for the "benzene ebulliometer" described by Osborn and Douslin (*14*). The air around the ebulliometer was circulated with a small squirrel-cage fan and was maintained within 1 K at temperatures from 50 to 100 K below the temperature of the boiling liquid. Also, the heat-transfer fluid previously used in the sample ebulliometer heater well was replaced with Monsanto Santovac 5 diffusion pump oil, which had been carefully outgassed.

For automated data acquisition, four platinum resistance thermometers with internally consistent calibrations were used for determining the boiling and condensation temperatures of the sample and the standard. The thermometers were read under computer control with an automatically balancing ac resistance bridge. The helium pressure was automatically set and controlled with a high-precision pressure controller.

***Inclined Piston Vapor Pressure Measurements.*** The equipment for these measurements has been extensively described (*21*, *22*). A recent revision of the procedures was to determine the balance angle of the piston from the rate of fall of the piston when the angle of inclination is slightly too large and from the rate of ascent when the angle is equally slightly too small. This greatly improves the accuracy and speed with which the balance angle can be determined relative to the former static method.

The equipment has been automated and operates under computer control. An automated angle adjustment and piston locating system were installed to the inclined piston gauge and were interfaced with the control computer. For angle adjustment, an inclinometer was mounted on top of the piston–cylinder assembly. The device generates a voltage in direct relation to the angle of inclination. The voltages are used with a stepping motor to monitor the angle to better than 10 s of arc. To track the piston position, a noncontacting linear displacement transducer (LDT) was attached to the end of the piston–cylinder assembly and a stainless steel target was placed on the moving piston. The LDT transducer generates a low-level inductive field in front of the sensor (probe). As the piston moves, the target enters or leaves this field, and eddy currents are generated in the target that change the impedance of the sensor. The output voltage from the transducer is linearly proportional to the distance from the piston to the conductive surface at the cylinder end.

The low-pressure range of the inclined piston measurements, 10–3500 Pa, necessitates diligent outgassing of the sample prior to introduction into the apparatus. Also, prior to sample introduction, all parts of the cell in contact with the sample were baked to 623 K under high vacuum. The thoroughly outgassed samples were then placed in the apparatus, and additional outgassing was done prior to commencing measurements. Finally, prior to each measurement, a small amount of the sample was pumped off. The measurements were made as a function of time to extrapolate the pressure to the time when the pumping valve was closed, i.e., to the time when insignificant amounts of light gas had leaked into the system or diffused out of the sample. The period when the sample space was refilling with vapor after pumping was disregarded in these extrapolations.

The null-point diaphragm (*22*) has an upper temperature limit for sensitivity set by the manufacturer of 473 K. In this work, the measurements on *n*-octacosane were made to 533 K, but the subsequent data analysis (see Comparison of *n*-Octacosane Data with Literature Values) has cast doubt on the data above 513 K.

## Results

***Experimental Results.*** The imprecision in the temperature measurements in both sets of apparatus was 0.001 K. In the ebulliometric vapor pressure measurements this gives a variance of

$$\sigma_i{}^2 = (0.001)^2\{(\mathrm{d}P_\chi/\mathrm{d}T)^2 + (\mathrm{d}P_{\mathrm{samp}}/\mathrm{d}T)^2\}$$

where $P_\chi$ is the vapor pressure of the reference substance (benzene for pressures less than 19 kPa and water for pressures greater than 19 kPa) and $P_{\mathrm{samp}}$ is the vapor pressure of the sample under study. The imprecisions in pressure for the reference substances are adequately described by $\sigma(P)/P = 4.07K^2/T^2$ and $\sigma(P)/P = 5.00K^2/T^2$, respectively.

For the *n*-octacosane ebulliometric measurements, *n*-decane replaced benzene as the low-pressure reference (for details see Use of *n*-Decane as a Secondary Standard). Here, the imprecision below 19 kPa is adequately described by the equation $\sigma(P)/P = 5.56K^2/T^2$.

The imprecision in pressure in the inclined piston vapor pressure measurements based on the estimated precision of measuring the mass, area, and angle of inclination of the piston is adequately described by $\sigma(P) = 0.172 + 0.000154P$, where $P$ is in Pa. The variance is $\sigma_i{}^2 = \sigma(P)^2 + (0.001K)^2(\mathrm{d}P_{\mathrm{samp}}/\mathrm{d}T)^2$.

In Tables I and II the vapor pressures obtained by using both sets of apparatus are reported for *n*-decane, *n*-eicosane, and *n*-octacosane. Following previous practice (*14*), the results obtained in the ebulliometric measurements were adjusted to common pressures. The adjusted temperatures for each of the *n*-alkanes are listed in Table I. For the ebulliometric points, the condensation temperatures are listed in column 3 of Table I, and the difference between the boiling and condensation temperatures for the sample are reported in column 4. A relatively

**Table I. Experimental Temperatures from Ebulliometric Vapor Pressure Measurements**

| standard | | | |
|---|---|---|---|
| substance[a] | $P^b$/kPa | $T_{cond}{}^c$/K | $(T_{boil} - T_{cond})^d$/K |
| | *n*-Decane | | |
| benzene | 9.596 | 373.236 | 0.005 |
| benzene | 10.897 | 376.467 | 0.005 |
| benzene | 12.348 | 379.711 | 0.004 |
| benzene | 13.961 | 382.970 | 0.003 |
| benzene | 15.752 | 386.240 | 0.003 |
| benzene | 17.737 | 389.523 | 0.003 |
| water | 19.933 | 392.820 | 0.003 |
| water | 25.023 | 399.449 | 0.002 |
| water | 31.177 | 406.133 | −0.001 |
| water | 38.565 | 412.866 | −0.002 |
| water | 47.375 | 419.652 | −0.001 |
| water | 57.817 | 426.489 | −0.001 |
| water | 70.120 | 433.377 | 0.000 |
| water | 84.533 | 440.317 | −0.001 |
| water | 101.325 | 447.307 | −0.001 |
| water | 120.79 | 454.349 | −0.001 |
| water | 143.25 | 461.441 | −0.002 |
| water | 169.02 | 468.580 | −0.002 |
| water | 198.49 | 475.772 | −0.002 |
| water | 232.02 | 483.009 | −0.001 |
| water | 270.02 | 490.292 | −0.001 |
| | *n*-Eicosane | | |
| benzene | 9.596 | 523.945 | 0.013 |
| benzene | 10.897 | 528.046 | 0.018 |
| benzene | 12.348 | 532.163 | 0.001 |
| benzene | 13.961 | 536.294 | 0.017 |
| benzene | 15.752 | 540.441 | 0.017 |
| benzene | 17.737 | 544.604 | 0.013 |
| water | 19.933 | 548.778 | 0.016 |
| water | 25.023 | 557.182 | 0.009 |
| water | 31.177 | 565.631 | 0.009 |
| water | 38.565 | 574.135 | 0.009 |
| water | 47.375 | 582.690 | 0.013 |
| water | 57.817 | 591.296 | 0.018 |
| water | 70.120 | 599.911 | 0.041[e] |
| water | 84.533 | 608.566 | 0.050[e] |
| water | 101.325 | 617.203 | 0.073[e] |
| water | 120.79 | 625.992 | 0.151[e] |
| | *n*-Octacosane | | |
| decane | 1.8786 | 554.455 | 0.333 |
| decane | 2.5742 | 563.251 | 0.202 |
| decane | 3.2945 | 570.411 | 0.174 |
| decane | 3.8847 | 575.337 | 0.163 |

[a] Substance in the reference ebulliometer. [b] Pressure calculated from the condensation temperature of the reference substance. [c] Condensation temperature of the sample. [d] The difference between the boiling and condensation temperatures for the sample. [e] The increase of this value suggests sample decomposition.

**Table II. Experimental Vapor Pressures from the Inclined Piston Measurements**

| $T$/K | $P$/kPa | $T$/K | $P$/kPa | $T$/K | $P$/kPa |
|---|---|---|---|---|---|
| | | *n*-Decane | | | |
| 268.148 | 0.0170 | 303.151 | 0.2561 | 323.150 | 0.8799 |
| 273.148 | 0.0264 | 308.149 | 0.3550 | 333.156 | 1.5238 |
| 283.144 | 0.0599 | 313.150 | 0.4863 | 343.152 | 2.5361 |
| 293.149 | 0.1276 | 318.149 | 0.6578 | 348.151 | 3.2271 |
| | | *n*-Eicosane | | | |
| 388.150 | 0.0156 | 413.150 | 0.0787 | 463.150 | 1.0077 |
| 393.151 | 0.0219 | 423.150 | 0.1399 | 473.150 | 1.5396 |
| 398.151 | 0.0307 | 443.150 | 0.3979 | 483.150 | 2.3003 |
| 403.150 | 0.0423 | 453.150 | 0.6419 | 488.150 | 2.7890 |
| 408.150 | 0.0583 | | | | |
| | | *n*-Octacosane | | | |
| 453.149 | 0.0131 | 483.150 | 0.0790 | 513.150 | 0.3517 |
| 463.151 | 0.0251 | 493.150 | 0.1345 | 523.151 | 0.5534[a] |
| 473.150 | 0.0460 | 503.150 | 0.2204 | 533.149 | 0.8318[a] |

[a] These values are of low precision due to apparatus limitations (see text).

**Table III. Cox Equation Constants and Fitting Parameters**

| | *n*-decane | *n*-eicosane | *n*-octacosane |
|---|---|---|---|
| $T_{ref}$/K | 447.307 ± 0.001 | 617.456 ± 0.016 | 705 ± 8 |
| $A$ | 2.96081 ± 0.00077 | 3.31018 ± 0.00811 | 3.41304 ± 0.03676 |
| $10^3B$/K$^{-1}$ | −1.90111 ± 0.00387 | −2.09536 ± 0.03298 | −1.88940 ± 0.13302 |
| $10^6C$/K$^{-2}$ | 1.60359 ± 0.00482 | 1.34198 ± 0.03396 | 1.04575 ± 0.12034 |
| data range/K | 268–490 | 388–626 | 453–575 |
| normalized covariance terms | | | |
| $AB$ | −0.99717 | −0.99915 | −0.99953 |
| $AC$ | 0.98953 | 0.99646 | 0.99821 |
| $BC$ | −0.99754 | −0.99906 | −0.99957 |

small difference between the boiling and condensation temperatures represents (a) correct operation of the equipment, and (b) a high-purity sample. For *n*-decane, and *n*-eicosane below 70 kPa, both criteria were fulfilled. However, *n*-eicosane underwent some sample decomposition above 70 kPa. GLC (gas–liquid chromatographic) analysis of the sample after completion of the measurements showed 3% impurity (the major impurity being *n*-tridecane). Experimental difficulties in obtaining a smooth-boiling sample are shown in the larger difference between $T_{boil}$ and $T_{cond}$ for *n*-octacosane. Sample decomposition, as indicated by ($T_{boil} - T_{cond}$) rising above 0.5 K, precluded measurements on *n*-octacosane at 4 kPa or above.

***Vapor Pressure Fits to the Cox Equation.*** Previous studies in this laboratory (*18*) have shown that the Cox equation (*23*) can adequately represent measured vapor pressure data from the triple-point pressure to 3 bar. Scott and Osborn (*5*) also showed the Antoine equation, the most commonly used to represent vapor pressure data, does not extrapolate well outside the experimental range. In contrast, the Cox equation extrapolates with reasonable precision over a 50 K range (*5*). The Cox equation was fitted to the vapor pressure data in the form

$$\ln (P/P_{ref}) = [1 - (T_{ref}/T)] \exp(A + BT + CT^2)$$

$P_{ref}$ was chosen as 101.325 kPa so that $T_{ref}$ was "the normal boiling point". In those fits, the sum of the weighted squares in the following function was minimized:

$$\Delta = \ln [\ln (P/P_{ref})/(1 - T_{ref}/T)] - A - BT - CT^2$$

The weighting factors, Wt, were the reciprocals of the variance in $\Delta$ derived from the propagation of errors in the temperature and pressure determinations. Wt is defined as

$$1/\mathrm{Wt} = (\delta\Delta/\delta T)_P{}^2[\sigma(T)]^2 + (\delta\Delta/\delta P)_P{}^2[\sigma(P)]^2$$

Parameters derived from the fits are given in Table III. For *n*-decane and *n*-eicosane, the normal boiling point was treated as an adjustable parameter. For *n*-octacosane, the experimental measurements did not approach the normal boiling point and an estimated value of 705 K (see below in Comparison of *n*-Octacosane Data with Literature Values) was used in the fit. The uncertainty in this estimate was assessed as ±8 K. Details of the fits of the Cox equation to the measured vapor pressures are given in Table IV.

***Enthalpies of Vaporization.*** Enthalpies of vaporization $\Delta_l^gH_m$ were derived from the Cox equation fits using the Clapeyron equation:

$$\mathrm{d}P/\mathrm{d}T = \Delta_l^gH_m/(T\Delta_l^gV_m)$$

where $\Delta_l^gH_m$ is the enthalpy of vaporization to the real vapor and $\Delta_l^gV_m$ is the increase in volume from the liquid to the real vapor. In the calculation of $\Delta_l^gV_m$, estimates of the second virial coefficient, $B$, were made by using the correlation de-

**Table IV. Deviations from Cox Equation Fits**

| $T$/K | $P_{\mathrm{obsd}}$/kPa | $P_{\mathrm{calcd}}$/kPa | $\Delta P$/kPa | $\sigma_i$/kPa |
|---|---|---|---|---|
| | | *n*-Decane | | |
| 268.148 | 0.0170 | 0.0169 | 0.0001 | 0.0002 |
| 273.148 | 0.0264 | 0.0263 | 0.0001 | 0.0002 |
| 283.144 | 0.0599 | 0.0599 | 0.0000 | 0.0002 |
| 293.149 | 0.1276 | 0.1277 | −0.0001 | 0.0002 |
| 303.151 | 0.2561 | 0.2560 | 0.0001 | 0.0002 |
| 308.149 | 0.3550 | 0.3551 | −0.0001 | 0.0002 |
| 313.150 | 0.4863 | 0.4862 | 0.0001 | 0.0002 |
| 318.149 | 0.6578 | 0.6577 | 0.0001 | 0.0003 |
| 323.150 | 0.8799 | 0.8797 | 0.0002 | 0.0003 |
| 333.156 | 1.5238 | 1.5237 | 0.0001 | 0.0004 |
| 343.152 | 2.5361 | 2.5356 | 0.0005 | 0.0006 |
| 348.151 | 3.2271 | 3.2269 | 0.0002 | 0.0007 |
| 373.236 | 9.596 | 9.594 | 0.001 | 0.0006 |
| 376.467 | 10.897 | 10.896 | 0.001 | 0.0007 |
| 379.711 | 12.348 | 12.347 | 0.001 | 0.0008 |
| 382.970 | 13.961 | 13.962 | −0.001 | 0.0008 |
| 386.240 | 15.752 | 15.753 | −0.001 | 0.0008 |
| 389.523 | 17.737 | 17.738 | −0.001 | 0.0010 |
| 392.820 | 19.933 | 19.934 | −0.001 | 0.0011 |
| 399.449 | 25.023 | 25.022 | 0.001 | 0.0014 |
| 406.133 | 31.177 | 31.178 | −0.001 | 0.0016 |
| 412.866 | 38.565 | 38.566 | −0.001 | 0.0020 |
| 419.652 | 47.375 | 47.378 | −0.003 | 0.0024 |
| 426.489 | 57.817 | 57.821 | −0.003 | 0.0028 |
| 433.377 | 70.120 | 70.124 | −0.003 | 0.0033 |
| 440.317 | 84.533 | 84.535 | −0.002 | 0.0038 |
| 447.307 | 101.325 | 101.324 | 0.001 | 0.0044 |
| 454.349 | 120.79 | 120.79 | 0.00 | 0.005 |
| 461.441 | 143.25 | 143.24 | 0.01 | 0.006 |
| 468.580 | 169.02 | 169.01 | 0.01 | 0.007 |
| 475.772 | 198.49 | 198.48 | 0.01 | 0.008 |
| 483.009 | 232.02 | 232.02 | 0.00 | 0.009 |
| 490.292 | 270.02 | 270.04 | −0.02 | 0.010 |
| | | *n*-Eicosane | | |
| 388.150 | 0.0156 | 0.0155 | 0.0001 | 0.0002 |
| 393.151 | 0.0219 | 0.0220 | −0.0001 | 0.0002 |
| 398.151 | 0.0307 | 0.0307 | 0.0000 | 0.0002 |
| 403.150 | 0.0423 | 0.0423 | 0.0000 | 0.0002 |
| 408.150 | 0.0583 | 0.0578 | 0.0005 | 0.0002 |
| 413.150 | 0.0787 | 0.0783 | 0.0004 | 0.0002 |
| 423.150 | 0.1399 | 0.1393 | 0.0006 | 0.0002 |
| 443.150 | 0.3979 | 0.3977 | 0.0002 | 0.0002 |
| 453.150 | 0.6419 | 0.6418 | 0.0001 | 0.0003 |
| 463.150 | 1.0077 | 1.0073 | 0.0004 | 0.0004 |
| 473.150 | 1.5396 | 1.5411 | −0.0015 | 0.0004 |
| 483.150 | 2.3003 | 2.3026 | −0.0023 | 0.0005 |
| 488.150 | 2.7890 | 2.7912 | −0.0022 | 0.0006 |
| 523.945 | 9.596 | 9.595 | 0.001 | 0.0005 |
| 528.046 | 10.897 | 10.896 | 0.001 | 0.0006 |
| 532.163 | 12.348 | 12.347 | 0.001 | 0.0008 |
| 536.294 | 13.961 | 13.960 | 0.001 | 0.0008 |
| 540.441 | 15.752 | 15.752 | 0.000 | 0.0008 |
| 544.604 | 17.737 | 17.737 | 0.000 | 0.0009 |
| 548.778 | 19.933 | 19.931 | 0.002 | 0.0011 |
| 557.182 | 25.023 | 25.027 | −0.004 | 0.0014 |
| 565.631 | 31.177 | 31.181 | −0.004 | 0.0016 |
| 574.135 | 38.565 | 38.569 | −0.004 | 0.0019 |
| 582.690 | 47.375 | 47.376 | −0.001 | 0.0022 |
| 591.296 | 57.817 | 57.809 | 0.008 | 0.0026 |
| 599.911 | 70.120 | 70.032 | 0.088$^a$ | 0.0032 |
| 608.566 | 84.533 | 84.317 | 0.216$^a$ | 0.0037 |
| 617.203 | 101.325 | 100.806 | 0.519$^a$ | 0.0042 |
| 625.992 | 120.79 | 120.13 | 0.66$^a$ | 0.005 |
| | | *n*-Octacosane | | |
| 453.149 | 0.0131 | 0.0140 | −0.0009 | 0.0002 |
| 463.151 | 0.0251 | 0.0260 | −0.0009 | 0.0002 |
| 473.150 | 0.0460 | 0.0464 | −0.0004 | 0.0002 |
| 483.150 | 0.0790 | 0.0802 | −0.0012 | 0.0002 |
| 493.150 | 0.1345 | 0.1346 | −0.0001 | 0.0002 |
| 503.150 | 0.2204 | 0.2198 | −0.0006 | 0.0002 |
| 513.150 | 0.3517 | 0.3497 | 0.0020 | 0.0002 |
| 523.151$^a$ | 0.5534 | 0.5433 | 0.0101 | 0.0003 |
| 533.149$^a$ | 0.8318 | 0.8252 | 0.0066 | 0.0003 |
| 554.455 | 1.8786 | 1.8788 | −0.0002 | 0.0001 |
| 563.251 | 2.5742 | 2.5744 | −0.0002 | 0.0002 |
| 570.411 | 3.2945 | 3.2943 | 0.0002 | 0.0002 |
| 575.337 | 3.8847 | 3.8845 | 0.0002 | 0.0002 |

[a] Point excluded in Cox fit (see text).

**Table V. Enthalpies of Vaporization Obtained from the Cox and Clapeyron Equations**

| $T$/K | $(\Delta_{\mathrm{l}}^{\mathrm{g}}H/R)$/K | $T$/K | $(\Delta_{\mathrm{l}}^{\mathrm{g}}H/R)$/K |
|---|---|---|---|
| | *n*-Decane | | |
| 260.000 | 6553 ± 9 | 380.000 | 5417 ± 15 |
| 280.000 | 6354 ± 5 | 400.000 | 5229 ± 24 |
| 290.000 | 6258 ± 3 | 420.000 | 5035 ± 36 |
| 298.150 | 6179 ± 2 | 440.000 | 4831 ± 53 |
| 300.000 | 6161 ± 2 | 460.000 | 4615 ± 75 |
| 320.000 | 5972 ± 2 | 480.000 | 4382 ± 101 |
| 340.000 | 5786 ± 4 | 500.000 | 4128 ± 135 |
| 360.000 | 5602 ± 8 | | |
| | *n*-Eicosane | | |
| 380.000 | 10713 ± 52 | 520.000 | 8510 ± 26 |
| 400.000 | 10360 ± 29 | 540.000 | 8212 ± 39 |
| 420.000 | 10037 ± 15 | 560.000 | 7907 ± 57 |
| 440.000 | 9716 ± 8 | 580.000 | 7592 ± 80 |
| 460.000 | 9406 ± 7 | 600.000 | 7261 ± 110 |
| 480.000 | 9103 ± 10 | 620.000 | 6909 ± 146 |
| 500.000 | 8806 ± 16 | | |
| | *n*-Octacosane | | |
| 440.000 | 13239 ± 241 | 540.000 | 11422 ± 12 |
| 460.000 | 12854 ± 134 | 560.000 | 11801 ± 17 |
| 480.000 | 12480 ± 68 | 580.000 | 10741 ± 28 |
| 500.000 | 12118 ± 32 | 600.000 | 10397 ± 43 |
| 520.000 | 11761 ± 16 | | |

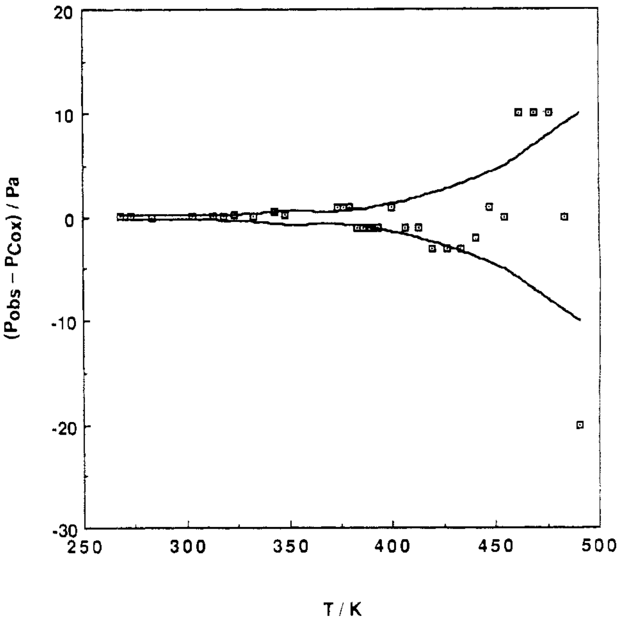

**Figure 1.** Deviation of experimental points from the Cox equation fit for *n*-decane. The solid line represents the variance (see text).

veloped by Scott et al. (*24*) and liquid densities were taken from the API 42 tables (*6*) or, in the case of *n*-decane, from unpublished values measured in this laboratory over the temperature range 300–423 K. For *n*-decane the second virial coefficient correlations of Lawrenson (*25*) and Tsonopoulos (*26*) gave essentially the same values of $B$ as those of the Scott correlation. The maximum deviation in the temperature range of application was 5% at 400 K. In the calculations, a 20% uncertainty was assigned to values of $B$ obtained by using the Scott et al. correlation. Derived enthalpies of vaporization are listed for each compound in Table V.

## Discussion

***Comparison of n-Decane Data with Literature Values.*** Figure 1 shows results from the fit of the Cox equation to our *n*-decane vapor pressures. The solid lines represent the variances tabulated in Table IV as calculated using the equations

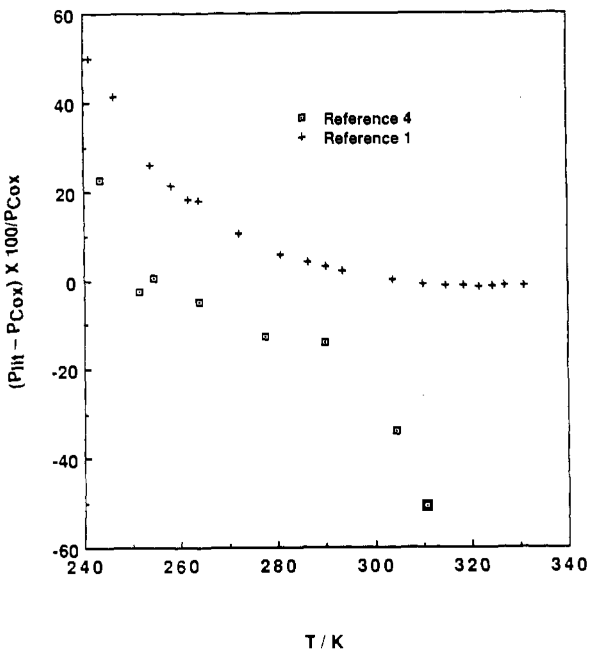

**Figure 2.** Comparison of literature low-pressure *n*-decane data with our measurements (Cox equation fit).

given above. Approximately 80% of the data points lie within the variance and all are fitted by the Cox equation within twice the variance.

Vapor pressures for *n*-decane have been measured by a number of researchers. The most quoted values are those due to Willingham et al. (*3*), Carruth and Kobayashi (*4*), and those tabulated in the TRC Tables (*1*). Figure 2 is a percentage deviation plot of the Carruth and Kobayashi values and low-pressure values (below 340 K) tabulated by TRC, relative to the Cox equation fit. The large percentage deviations are disturbing, especially since the higher pressure data reported here are in excellent agreement with those given by Willingham et al. The largest deviation, 0.1%, between the vapor pressures reported here and those of Willingham et al. occurs at 7.65 kPa. In an attempt to find a thermodynamically consistent set of vapor pressures for *n*-decane, the so-called "third-law" method was employed. The "third-law" values were calculated from the tabulated thermodynamic functions of the ideal gas (*27*) and the liquid (*28*), at 243.50 K (the triple point), 273.15 K, and 298.15 K, and the enthalpy of vaporization determined at 298.15 K (*29*). The relevant equation is

$$-R \ln (f_g/a_l) = \{(G^\circ - H^\circ_{298})/T\}_g - \{(G^\circ - H^\circ_{298})/T\}_l + \Delta_l^g H^\circ_{298}/T$$

where $f_g$ is the fugacity of the gas phase and $a_l$ the activity of the liquid phase, respectively. The ratio $(f_g/a_l)$ was assumed to equal $P$, the vapor pressure. This assumption is valid at the low pressures considered here.

The calculated pressures at 243.50, 273.15, and 298.15 K were 0.0013, 0.0264, and 0.1823 kPa, respectively. These values are in good agreement with those calculated by using the Cox equation constants, 0.0014, 0.0263, and 0.1821 kPa, respectively.

An additional consistency test was performed by comparing the calculated enthalpy of vaporization at 298.15 K, (6179 ± 2)$R$/K, with the experimentally reported value, (*29*): 6177$R$/K. Again, agreement is excellent.

A value of 6177$R$ is obtained for the enthalpy of vaporization by using the data of Carruth and Kobayashi (*4*), but this applies at the midpoint of the temperature range of their data, 277 K. Figure 3 is a plot that compares the enthalpy of vaporization of *n*-decane obtained in this research (Table V) with the experimental data of Couch et al. (*30*). The agreement is good, particularly at the low-temperature end of the data.

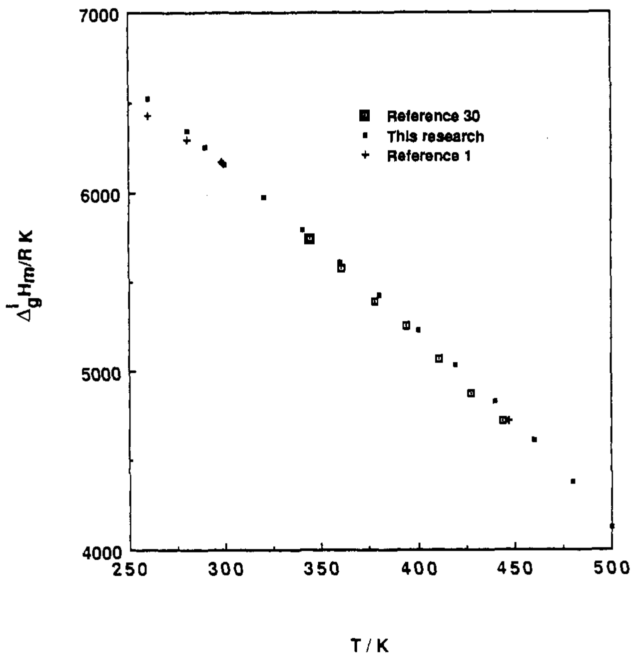

**Figure 3.** Comparison of enthalpies of vaporization for *n*-decane with literature values.

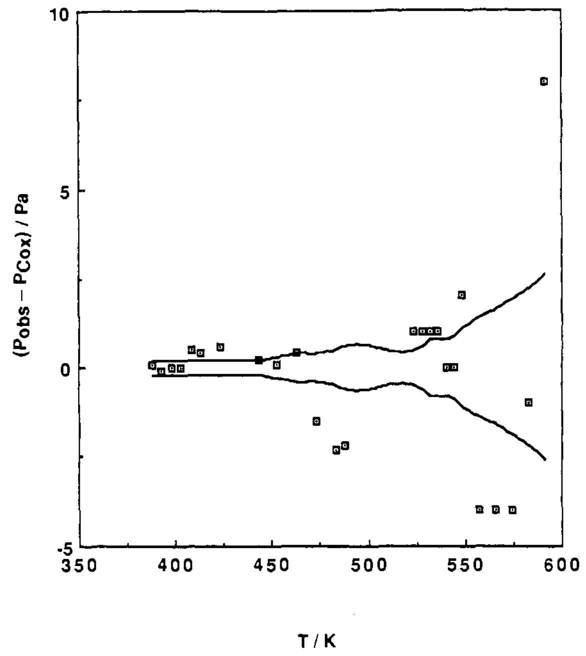

**Figure 4.** Deviation of experimental points from the Cox equation fit for *n*-eicosane. The solid line represents the variance (see text).

Also included in Figure 3 are enthalpies of vaporization derived from the TRC (*1*) reported vapor pressures. At the low-temperature end the derived enthalpies of vaporization are up to 100$R$ lower than those given here.

These consistency tests show that both the tabulated low-pressure (below 300 K) TRC values and those reported by Carruth and Kobayashi (*4*) are in error. Above 260 K, the gas-saturation data of Carruth and Kobayashi show incomplete saturation of the gas phase. Apparently TRC gave too much weight to the gas-saturation data near the triple point. Similar concerns about the data of Carruth and Kobayashi for the $C_2$–$C_4$ *n*-alkanes have been raised by NBS (*31*–*33*).

***Comparison of n-Eicosane Data with Literature Values.*** Figure 4 shows a deviation plot of our vapor pressures for

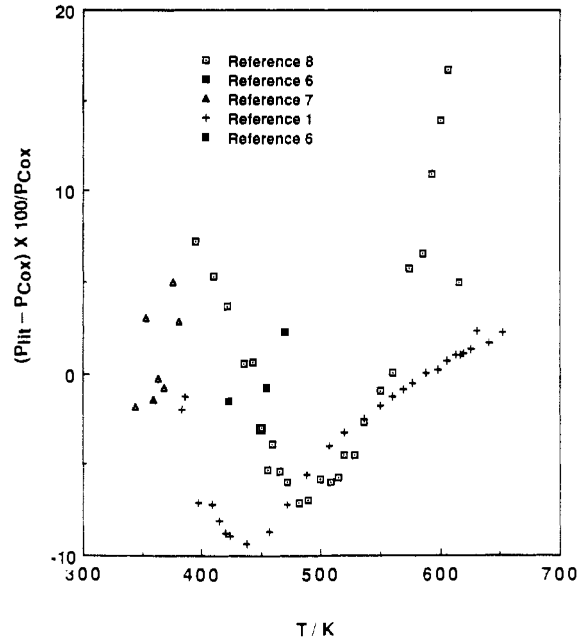

**Figure 5.** Comparison of literature *n*-eicosane vapor pressure data with our measurements (Cox equation fit).

*n*-eicosane relative to the Cox equation fit. The data set shows a few outlying points, but the majority lie within twice the standard deviation. Hence, the Cox equation gives a good representation of the experimental data. Figure 5 shows percentage deviation plots for the vapor pressure data of Myers and Fenske (*8*), Macknick and Prausnitz (*7*), API 42 (*6*), and the TRC tables, (*1*), relative to our Cox equation fit for *n*-eicosane. The data of Macknick and Prausnitz (*7*) were obtained by using a gas-saturation technique similar to that used by Carruth and Kobayashi (*4*) for *n*-decane. However, in contrast to the latter study, gas saturation seems to have been achieved. The data were all obtained at lower pressures than those reported here and are in accord with values calculated by extrapolation using our fitted Cox equation constants (Table III). The maximum percentage deviation obtained relative to the Cox fit was 5.0% at 376.1 K, 0.0064 kPa (calculated) versus 0.0067 kPa (measured).

The five values given in API 42 (*6*) are also in reasonable agreement with our results. The percentage deviations from the Cox fit are −1.5% and 0.2% at 0.1333 and 1.333 kPa, respectively. The API 42 tables list an enthalpy of vaporization for *n*-eicosane of 9812*R*/K. This value was "was calculated from boiling points at 0.5 and 10 mm using Clausius–Clapeyron equation." Hence, the value applied at the midpoint of that temperature range, 440 K, is in fair agreement with our value (Table V) of (9716 ± 8)*R*/K.

The vapor pressure data of Myers and Fenske (*8*) show a systematic deviation from those obtained here. The deviations at the high-temperature end may be due to sample decomposition, as was noted above in the Experimental Section. The usual explanation for "high" vapor pressure values at low temperature is an impure sample, but in this case some of the reported data are actually lower than our measurements. A possible explanation of the deviations could be incorrect thermometer calibration. This hypothesis can be checked by comparing the data of Myers and Fenske (*8*) for other compounds that have been carefully investigated.

The tabulated TRC values (*1*) show a systematic trend, when compared with the values obtained in our research. Where a direct comparison can be made, the deviations of their tabulated pressures from our corresponding pressures calculated using the Cox equation constants range from −2% at 383 K through a minimum of −9.4% at 437 K to +1% at 606 K.

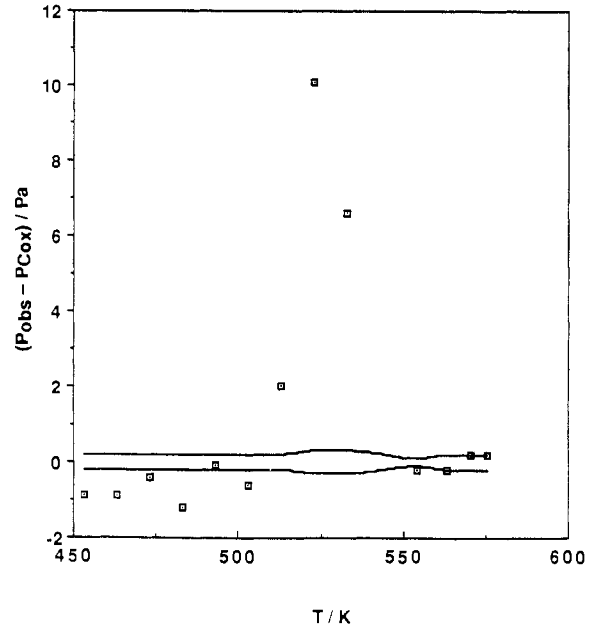

**Figure 6.** Deviation of experimental points from the Cox equation fit for *n*-octacosane. The solid line represents the variance (see text).

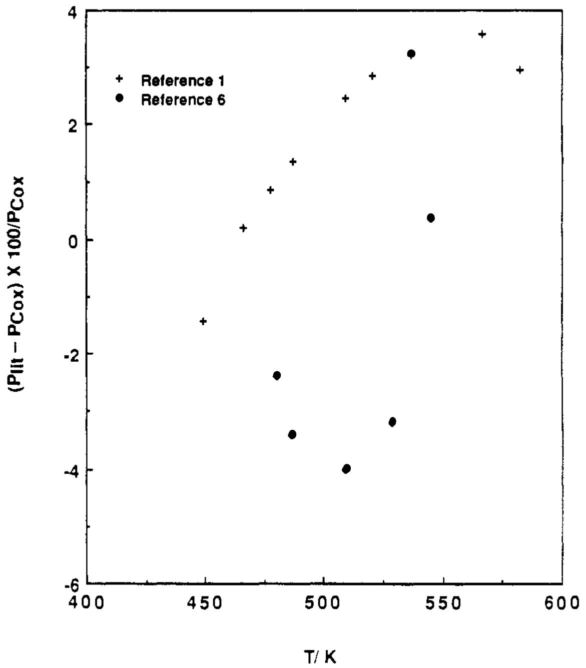

**Figure 7.** Comparison of literature low-pressure *n*-octacosane data with our measurements (Cox equation fit).

Our value for the normal boiling point of *n*-eicosane, (617.456 ± 0.016)K, obtained by treating it as an adjustable parameter in the Cox equation fit, is higher than the tabulated TRC value (*1*), 616.95 K, or that obtained by using the Kreglewski and Zwolinski (*34*) correlation, 617.13 K.

***Comparison of n-Octacosane Data with Literature Values.*** Figure 6 shows a deviation plot of our vapor pressures for *n*-octacosane relative to the Cox equation fit. The boiling point used in the Cox equation fit, 705 K, was obtained by using the Kreglewski and Zwolinski (*34*) correlation. The Cox equation provides good representation of the reported experimental data. The relatively large deviations between the observed and calculated values at 523 and 533 K (see Table IV) are due to loss of sensitivity of the null-point diaphragm in the inclined piston apparatus.

Figure 7 shows percentage deviation plots of the API 42 (*6*) and TRC (*1*) values relative to the Cox fit. The API 42 values

**Table VI. Vapor Pressures of Ebulliometric Standards**

| $T$/K | $P$/kPa | $T$/K | $P$/kPa | $T$/K | $P$/kPa |
|---|---|---|---|---|---|
| | | Benzene | | | |
| 292.221 | 9.596 | 297.546 | 12.348 | 302.915 | 15.752 |
| 294.878 | 10.897 | 300.225 | 13.961 | 305.617 | 17.737 |
| | | Water | | | |
| 333.150 | 19.933 | 358.150 | 57.817 | 383.150 | 143.25 |
| 338.150 | 25.023 | 363.150 | 70.120 | 388.150 | 169.02 |
| 343.150 | 31.177 | 368.150 | 84.533 | 393.150 | 198.49 |
| 348.150 | 38.565 | 373.150 | 101.325 | 398.150 | 232.02 |
| 353.150 | 47.375 | 378.150 | 120.79 | 403.150 | 270.02 |
| | | *n*-Decane | | | |
| 338.402 | 2.000 | 368.742 | 7.999 | 387.792 | 16.665 |
| 344.181 | 2.666 | 375.925 | 10.666 | 392.823 | 19.933 |
| 352.759 | 4.000 | 381.743 | 13.332 | 399.453 | 25.023 |
| 359.179 | 5.333 | | | | |

are in reasonable agreement with the data reported here: at 528.65 K, the vapor pressure value is 0.667 kPa compared with a calculated Cox equation value of 0.685 kPa; and at 545.15 K, it is 1.333 kPa compared with a calculated value of 1.326 kPa. The API 42 tables list an enthalpy of vaporization for *n*-octacosane of 12119$R$/K at 510 K. The value is in fair agreement with (11940 ± 6)$R$/K obtained in this research (see Table V). The tabulated TRC values are those obtained by using the Antoine correlation derived by Kudchadker and Zwolinski (*34*) and are in fair agreement with our measurements. This places confidence in using the correlation to calculate vapor pressures (within ±10%) for *n*-alkanes in the range $C_{20}$ to at least $C_{28}$ when measured values are nonexistent or are of poor quality.

***Use of n-Decane as a Secondary Standard in Comparative Ebulliometry.*** In comparative ebulliometry, the standard compounds are typically benzene and water. Water was not used in our apparatus below a pressure of 19 kPa due to problems in obtaining smooth boiling. Benzene was used below 19 kPa as the standard, but the lower limit of its applicability is set by its freezing point at 278.7 K; the lowest operating pressure is approximately 9.6 kPa. The upper pressure limit in our inclined piston apparatus in its present configuration is approximately 3.5 kPa. Hence, there is a gap between the pressure ranges spanned by the two apparatus. Measurements using the inclined piston are subject to the usual uncertainties associated with static vapor pressure measurement, namely, the problem of knowing if light gases have been removed completely before data are taken. Therefore, an overlap region between both sets of apparatus would serve as a valuable cross-check. The use of *n*-decane as a secondary standard for the ebulliometric measurements fulfills this need. The excellent agreement between the experimental data reported here and those of Willingham et al. (*3*), plus the corroboration obtained using the "third-law" calculations, meet the requirements of a secondary standard (*35*). Table VI lists the standard temperatures/pressures in use in this laboratory for comparative ebulliometric measurements using benzene, water, and now *n*-decane as standard reference substances.

## Conclusions

The following conclusions are made on the basis of the new, reliable vapor pressures for *n*-decane, *n*-eicosane, and *n*-octacosane:

1. *n*-Decane has been established as a new secondary standard for comparison ebulliometry.
2. The Cox equation gives a good representation of the vapor pressure of *n*-alkanes over the range from the triple point to the normal boiling point.
3. The vapor pressures in the API 42 tables are of reasonable accuracy.
4. In contrast, the tabulated TRC vapor pressures for both *n*-decane (below 300 K) and *n*-eicosane need revision.
5. The *n*-decane vapor pressures of Carruth and Kobayashi (*4*) are in error.
6. The *n*-eicosane vapor pressures of Myers and Fenske (*8*) also show a systematic error.

## Acknowledgment

We thank John L. Heidman for his support and comments on the manuscript.

## Glossary

| | |
|---|---|
| $a$ | activity |
| $A, B, C$ | Cox equation constants |
| $B$ | the second virial coefficient |
| $f$ | fugacity of the gas phase |
| $G$ | molar Gibbs energy, J·mol$^{-1}$ |
| $P$ | pressure, Pa or kPa |
| $R$ | gas constant (8.314 41 J·K$^{-1}$·mol$^{-1}$) |
| $T$ | temperature, K |
| $V$ | molal volume, cm$^3$·mol$^{-1}$ |
| Wt | weighting factor |

*Greek Symbols*

| | |
|---|---|
| $\Delta$ | difference |
| $\Delta_l^g M$ | difference between gas and liquid property $M$ (at same $T$ and $P$) |
| $\sigma_i$ | variance in the point $i$ |
| $\chi$ | property (pressure) of reference substance in ebulliometer |

*Subscripts*

| | |
|---|---|
| boil | boiling (temperature) |
| calcd | calculated value (pressure) |
| cond | condensation (temperature) |
| Cox | (pressure) calculated with Cox equation |
| g | (real) gas property |
| l | liquid property |
| lit | literature value (pressure) |
| obsd | observed value (pressure) |
| ref | property of reference substance |
| samp | property of sample investigated |
| 298 | property at 298.15 K |

*Superscripts*

| | |
|---|---|
| $\circ$ | property at standard state |

## Literature Cited

(1) *TRC Thermodynamic Tables—Hydrocarbons* (Formerly API Research Project 44, then TRC Hydrocarbon Project. Selected Values of Properties of Hydrocarbons and Related Compounds, Category A. Tables of Physical and Thermodynamic Properties; available under subscription with updates; Thermodynamics Research Center: Texas A&M University, College Station, TX, sheets extant 1988.

(2) Kudchadker, A. P.; Zwolinski, B. J. *J. Chem. Eng. Data* **1966**, *11*, 253.

(3) Willingham, C. B.; Taylor, W. J.; Pignocco, J. M.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* **1945**, *35*, 219.

(4) Carruth, G. F.; Kobayashi, R. *J. Chem. Eng. Data* **1973**, *18*, 115.

(5) Scott, D. W.; Osborn, A. G. *J. Phys. Chem.* **1979**, *83*, 2714.

(6) *API Research Project 42. Properties of Hydrocarbons of High Molecular Weight*; Pennsylvania State University: University Park, PA, 1966.

(7) Macknick, A. B.; Prausnitz, J. M. *J. Chem. Eng. Data* **1979**, *24*, 175.

(8) Myers, H. S.; Fenske, M. R. *Ind. Eng. Chem.* **1955**, *47*, 1652.

(9) CODATA 1977. The 1969 atomic weights were used because the CODATA Recommended Key Values for Thermodynamics of 1977 are based on these atomic weights. See *J. Chem. Thermodyn.* **1976**, *10*, 903.

(10) Commission on Atomic Weights *Pure Appl. Chem.* **1970**, *21*, 93.

(11) *CODATA Bull.* **1978**, *No. 28*.

(12) Comite International des Poids et Measures *Metrologia*, **1969**, *5*, 35.

(13) Swietoslawski, W. *Ebulliometric Measurements*; Reinhold: New York, 1945.

(14) Osborn, A. G.; Douslin, D. R. *J. Chem. Eng. Data* **1966**, *11*, 502.

(15) Osborne, N. S.; Stimson, H. F.; Ginnings, D. C. *J. Res. Natl. Bur. Stand.* **1939**, *23*, 261.

(16) Stimson, H. F. *J. Res. Natl. Bur. Stand.* **1969**, *73A*, 493.
(17) Osborn, A. G.; Douslin, D. R. *J. Chem. Eng. Data* **1974**, *19*, 114.
(18) Osborn, A. G.; Scott, D. W. *J. Chem. Thermodyn.* **1976**, *10*, 619.
(19) Forziati, A. F.; Norris, W. R.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* **1949**, *43*, 555.
(20) Todd, S. S.; Hossenlopp, I. A.; Scott, D. W. *J. Chem. Thermodyn.* **1978**, *10*, 641.
(21) Douslin, D. R.; McCullough, J. P. *U.S. Bur. Mines* **1963**, *RI 6149*.
(22) Douslin, D. R.; Osborn, A. G. *J. Sci. Instrum.* **1965**, *42*, 369.
(23) Cox, E. R. *Ind. Eng. Chem.* **1936**, *28*, 613.
(24) Scott, D. W.; Finke, H. L.; Gross, M. E.; Guthrie, G. B.; Huffman, H. M. *J. Am. Chem. Soc.* **1950**, *72*, 2424.
(25) Lawrenson, I. J. *NPL Rep. Chem.* (*U.K., Natl. Phys. Lab., Div. Chem. Stand.*) **1977**; *No. 62*.
(26) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(27) Scott, D. W. *U.S. Bur. Mines Bull.* **1974**, *No. 666*.
(28) Messerly, J. F.; Guthrie, G. B.; Todd, S. S.; Finke, H. L. *J. Chem. Eng. Data* **1967**, *12*, 338.
(29) Osborne, N. S.; Ginnings, D. C. *J. Res. Natl. Bur. Stand.* **1947**, *39*, 453.
(30) Couch, H. T.; Kozicki, W.; Sage, B. H. *J. Chem. Eng. Data* **1963**, *8*, 346.
(31) Goodwin, R. D.; Haynes, W. M. *Thermophysical Properties of Propane from 85 K to 700 K at Pressures to 70 MPa*; NBS Monograph 170; U.S. Department of Commerce: Washington, DC, April 1982.
(32) Goodwin, R. D.; Roder, H. M.; Straty, G. C. *Thermophysical Properties of Ethane, from 90 K to 600 K at Pressures to 700 bar*; NBS Technical Note 684; U.S. Department of Commerce: Washington, DC, August 1976.
(33) Haynes, W. M.; Goodwin, R. D. *Thermophysical Properties of Normal Butane from 135 to 700 K at Pressures to 70 MPa*; NBS Monograph 169; U.S. Department of Commerce, Washington, DC, April 1982.
(34) Kreglewski, A.; Zwolinski, B. J. *J. Phys. Chem.* **1961**, *65*, 1050.
(35) Ambrose, D. *NPL Report Chem.* (*U.K. Natl. Phys. Lab., Div. Chem. Stand.*) **1977**; *No. 67*.

Received for review March 14, 1988. Revised October 17, 1988. Accepted October 25, 1988. The financial support of Exxon Research and Engineering Company is gratefully acknowledged.

---

# Equilibrium Adsorption of Methane, Ethane, Ethylene, and Propylene and Their Mixtures on Activated Carbon

**E. Costa, G. Calleja,* C. Marrón, A. Jiménez, and J. Pau**

*Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain*

**Pure gas adsorption isotherms of methane, ethane, ethylene, and propylene on activated carbon have been determined at 323 K and pressures in the range 0–100 kPa. Binary and ternary adsorption isotherms were also determined at the same temperature and pressures for all the mixtures of these adsorbates, with the exception of methane–propylene mixtures due to their difference in adsorption capacity. Two models have been applied for correlation and prediction of mixture adsorption equilibria—the ideal adsorbed solution (IAS) and the real adsorbed solution (RAS). This second model provides better results for all the systems.**

## Introduction

Equilibrium adsorption data for mixtures in heterogeneous adsorbents, like activated carbon, are relatively scarce in the literature, existing only a few studies for binary, ternary, and higher order mixtures (*1*–*3*). However, the interest in these mixture equilibria is evident, new accurate data being necessary to validate theoretical models and providing a stronger scientific basis for industrial design.

In a previous paper (*3*) we reported adsorption equilibrium data of light hydrocarbons, methane, ethane, ethylene, and propylene and their mixtures, on a commercial activated carbon, at 293 K. We now present the experimental data corresponding to the same hydrocarbons and their binary and ternary mixtures on the same carbon at a higher temperature, 323 K. All mixtures have been studied, with the exception of binary and ternary mixtures having together methane and propylene, since their adsorption capacity is so different that an uncertain extrapolation of the isotherms would be necessary to calculate spreading pressures of the mixtures.

Among the different models available in the literature for predicting mixture adsorption equilibria (*3*–*8*) we have applied in this study the ideal adsorbed solution (IAS) by Myers and Prausnitz (*4*) and the real adsorbed solution (RAS) previously used by Costa et al. (*3*, *9*), also known as nonideal adsorbed solution.

## Experimental Section

***Apparatus*.** The apparatus was of the volumetric type, and was described in detail in previous works (*3*, *10*). Basically it consists of a glass closed circuit with a fixed bed of adsorbent, a membrane compressor for gas circulation, and a volumetric system to introduce and measure the gases admitted, by appropriate $P-V-T$ measurements. The analysis of the gas phase was done by gas chromatography, and the adsorbed phase composition was determined by mass balance from the initial and equilibrium composition of the gas phase. These experiments were performed at 323 K.

***Materials*.** The adsorbent used was a commercial activated carbon, AC-40, from CECA (Comañia Española de Carbón Activo, S.A.), previously used in other adsorption studies (*3*), with a BET surface of 700 $m^2/g$ and a particle porosity of 0.715. The particles had a cylindrical shape of 0.83-mm radius and 4.26-mm height and real and apparent densities of 2700 and 795 $kg/m^3$, respectively. Regeneration, drying and manipulation conditions of the carbon were the same as described previously (*3*).

Gaseous hydrocarbons used as adsorbates were methane, ethane, ethylene, and propylene, provided by SEO (Sociedad Española de Oxígeno), with a purity higher than 99% in all cases.

## Pure-Component Data

The experimental equilibrium isotherms for the pure components methane, ethane, ethylene, and propylene on activated carbon are shown in Table I, at a temperature of 323 K and pressures up to 100 kPa. Curves corresponding to these isotherms are shown in Figure 1, where they can also be compared with the corresponding adsorption isotherms at 293 K,

---

* Author to whom correspondence should be addressed.