calculations were made using the estimated heat capacities of calculations were made using the estimated heat capacities of
Schafer and Kahlenberg (5), viz., $C_p(g) = 31.6 - 3.7 \times 10^{10}$
10. The standard onthelps: Schafer and Kahlenberg (5), viz., $C_p(g) = 31.6 - 3.7 \times 10^5/T^2$ and $C_p(s) = 38 - 3 \times 10^5/T^2$. The standard enthalpy and entropy of sublimation values at 298 were calculated to be $\Delta H_{298}^{\circ} = 22.1$ kcal/g-mol and $\Delta S_{298}^{\circ} = 44.8$ eu, respectively. The equation, $\log_{10} P_{\text{mm}} = (12.03 \pm 1.86) - (4604 \pm 1.86)$ 40 / T was obtained by a least-squares fit of the experimental data and is shown in Table I1 along with enthalpies and entropies of vaporization at the mean temperature and at 298 for comparison with similar values of previous investigators.

DISCUSSION

The heat of sublimation obtained in this work compares favorably with the values reported by both Saeki et al. *(4)* and Schafer and Kahlenberg *(5)* as noted in Table I1 while the vapor-pressure values are in reasonably close agreement only with Saeki's (less than 5% difference at the mean temperature). The vapor pressure of Shchukarev and Kurbanov (7) is 14% lower than reported in this paper while the vapor pressure calculated from the equation of Schafer and Kahlenberg is approximately 15% higher.

No experimental heat capacity data were found in the literature; consequently, only estimates of the standard enthalpy and entropy at 298 could be made. The uncertainties of the estimated heat capacities of Schafer and Kahlenberg is probably greater than the experimental uncertainty as given

for ΔH_T° . The true values of ΔH_{298}° and ΔS_{298}° are estimated to be within **3-5%** of those reported.

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Surface Properties of Nine Liquids

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The surface energy, the surface entropy, and the latent heat of surface formation, all per unit area, have been calculated for nine pure liquid-air systems from information on surface tension as a linear function of temperature. For seven of the liquidswater, benzene, n-butanol, methyl propyl ketone, isooctane, diisopropyl ether, diisobutyl ketone-experimental surface tension measurements are presented at 20, **30,** 40, and **5OoC.** This information has been augmented by selected values from the literature and by equations derived to express surface tension as a function of temperature. For toluene and carbon tetrachloride, all the information was taken from the literature. To about 1 part in 1000 at least, the surface energies per unit area of the reported liquids are constant over a range of about **100°C.** Two new equations are derived to predict the surface tension of benzene over its normal liquid range. These equations, representing a consensus of much work, predict for benzene at *20'C* that $\sigma=$ 28.88 dyn/cm, thus confirming the accepted standard value proposed by Harkins in 1945.

If data are available on the surface tension of a liquid-gas systern over an appreciable range of temperature, it is possible to calculate several significant surface properties, such as the latent heat and the entropy of formation of a fresh unit of surface. Unfortunately, rarely is surface tension measured over a significant temperature range. Accordingly, when suitable experimental data became available on seven liquids, the ther-

modynamic properties were derived by conventional surface thermodynamics. At the same time, an assessment of literature data on two additional liquids made it possible to raise the number of substances thus evaluated to nine.

EXPERIMENTAL

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Seven liquids-water, benzene, isooctane, n -butyl alcohol, methyl propyl ketone, diisopropyl ether, and diisobutyl

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ketone-were carefully purified by various appropriate means, as described by Bonnet *(7)* and by Pike and Bonnet *(55).* The physical properties of the final purified chemicals are presented in Table I. The properties of the water, benzene, n-butyl alcohol, isooctane, and methyl propyl ketone agreed closely with established values, giving assurance that these chemicals were of excellent purity. In the case of diisobutyl ketone, the possibility of isomers clouds the issue somewhat, but it, too, was judged to be of high purity. In the case of isopropyl ether, even though it was carefully dehydrated and distilled, its quality remained suspect.

The surface tension measurements were made by Bonnet *(7)* at 20° , 30° , 40° , and 50° C, employing the Wilhelmy technique with a roughened glass plate 2.199 cm long and 0.015 cm thick.

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The apparatus employed was a Rosano Surface Tensiometer, marketed by the Roller Smith Division of the Federal Pacific Electric Co., h'orthborough, Mass. While excellent for its purpose as a rapid, routine, laboratory instrument, it is not primarily a research instrument. As employed with repeated measurements, it provided a standard deviation of 0.25, 0.11, and 0.07 dyn/cm at the levels of 70, **30,** and 20 dyn/cm. End corrections were calculated and applied according to the procedure of Pike and Bonnet *(55).* Also, the meniscus correction of Kawanishi et al. (39) was applied. The final experimental surface tension values are presented in Table 11, along with predictions based upon the equations presented in Table 111.

DERIVED SURFACE TENSION CORRELATIONS

The experimental surface tension data were assessed against, and augmented with, published values within the temperature ranges of Table 111. This is a judgment problem of some difficulty since surface tension measurements are extraordinarily prone to errors due to contamination. A problem develops, too, in that the mathematical models needed for treatment of data took years to develop and many versions were used. Particularly in the past, these problems have not always been appreciated and wrong models were employed even though obsolete. This had led to some recalculation by various authors, but not enough. Even so, when an appreciable inventory of measurements were available (such as for benzene), it was possible to separate out with reasonable confidence a consistent band of data defining the relationship with respect to temperature. In making the present judgment, reliance was placed on the measurements of this research to make the primary value judgments on what classes of reported results to reject. Interestingly, Harkins (30) argued that most of the data obtained before 1916 are in error, thus suggesting a separation of data based upon age. Morino *(48),* however, noticed for benzene the same separation of data as we do into a recognizably valid class and another class with its own internal consistency. Fortunately, the procedure was not as ambiguous as would appear. In general, the band of surface tension values accepted possessed a band width of about ± 0.15 dyn/cm, while the rejected values differed from the relationship accepted by 0.7-1.2 dyn/cm. Finally, the accepted values were fitted by the method of least squares to the linear equations required by the thermodynamic analysis. However, in addition, the same set of data was also fitted to quadratic equations in an effort to improve the degree of fit.

The two derived algebraic relationships between surface tension and temperature are presented in Table 111, along with the coefficient of determination, and the 95% confidence range at the mean (for the linear fit). **A** statistical analysis of variance demonstrated that the linear equations adequately fitted the data and that the quadratic equations gave only a slight, statistically insignificant, improvement.

For the benzene-air system, the selection scheme outlined retained **127** data points and discarded 90. Corrections to the liquid-air basis were taken from the ICT *(37).* Those

Table 111. Surface Tension as Function of Temperature

^a Sums of squares due to regression divided by the sums of squares about the mean. **At** the mean value of the surface tension in dyn/cm.

points retained were taken from this research (Table 11) plus refs. *1-6, 9-11, 18, 19, 21-23, 28, 32-36, 40-43, 48, 50, 52, 54,* refs. 63 and *89* as recalculated by refs. *83* and *77.* These represent 56 separate sources. The selected data occupy a linear band with a width of about $\pm 0.15 \,\mathrm{dyn/cm}$. In contrast, most of the rejected data were lower by about $0.5-1.2$ dyn/cm. The obvious differences greatly simplified the selection problem. Benzene occupies a special position in surface tension work, in part because of its ease of purification, and often serves as a secondary surface tension standard. The generally accepted value is 28.88 dyn/cm at 20° C, as recommended by Harkins *(SO).* The special history of benzene as a secondary standard has imparted a peculiar bias to the reported results. Measurements at temperatures different from 20°C are often based upon a calibration to read $\sigma = 28.88$ at 20°C. Even when the results are ostensibly independent, the reputation of Harkins seems to impose values close to 28.88 at $t = 20^{\circ}$ C. It comes as no surprise, then, that the linear equation derived here predicts 28.886 dyn/cm while the quadratic equation predicts 28.879 and a cubic fit predicts 28.883. **A** consensus prediction of 28.88 seems appropriate. Yet away from 20° C, these equations diverge from that of Harkins up to 0.2 dyn/cm at 0° C. For the linear equation the predictions possess 95% confidence limits at 5.5°, 10°, 20°, 30°, 40°, 50°, 60°, 70°, and 80° C of ± 0.060 , 0.053, 0.039, 0.032, 0.035, 0.046, 0.061, 0.078, and 0.096 dyn/cm. The agreement between the equations derived here and the 1926 equation of Harkins is close enough (average about 0.05 dyn/cm) to lend confidence to the present procedure of classifying the published values into acceptable and nonacceptable groups. *58-60, 621 64-70, 72, 74-77, 79-81, 84, 85, 87, 88, 91* , *93* plus

For the n-butanol-air system, the 35 data points retained comprise those of this research (Table 11) plus refs. *8,* **20,** *34, 36, 45, 51, 70, 82.* The 15 discarded points were either about 0.7 dyn/cm high or 0.3-0.6 dyn/cm lower than the accepted band. As shown in Table 11, the present experimental data agree with the final correlation within ± 0.05 dyn/cm on the average.

For the diisopropyl ether-air system, there were only six accepted data points, those of this research (Table 11) and two of Vogel's *(86).* These agree very well. Two other data points were discarded.

For the methyl propyl ketone (2 pentanone)-air system, the 19 data points retained were 10 points calculated from 0-100°C

from Wright *(92)* plus those of this research (Table 11) and refs. 53,56.

For isooctane **(2,2,4** trimethyl pentane)-air, the 18 accepted data points (none discarded) were taken from this research (Table 11) and refs. *17, 21, 46, 66, 69, 90.* The measurements of Bonnet were about 1% higher than the others, which agreed closely among themselves. The differences being slight, the entire set was treated in the usual manner by the method of least squares.

In regard to the diisobutyl ketone (2,6 dimethyl **4** heptanone)-air system, only one set of literature values was located, those of Cowan et al. *(13).* Their measurements differed from those of this research (Table 11), both in magnitude and in slope with respect to temperature.

The equations presented in Table I11 are based solely on Table I1 data.

For the carbon tetrachloride-air system, the literature values were very discordant and presented a difficult choice. The 42 data points finally accepted were from refs. *1, 4, 6, 8, 16, 29, 31, 33, 341 36, 40, 48, 50, 62, 68, 80, 89, 93* plus ref. *58* as recalculated by Sugden *(77).* Corrections to the liquid-air basis were taken from the ICT *(37).* The discarded points numbered 71 and presented an unusual pattern. One portion roughly followed a line about 0.7 dyn/cm higher than the central band, while the rest were similarly placed about 1.2 dyn/cm lower than the central band. In contrast, the accepted central band was quite consistent, with a standard deviation at the mean of 0.05 dyn/cm.

For the toluene-air system, 58 acceptable data points were collected from refs. *1* , *3, 4, 8, 11, 14, 18, 23, 26, 36, 42, 43, 47, 48, 60, 58, 59, 67, 68, 73, 81* , *86-88* plus ref. *89* recalculated by Sugden (78). Corrections to the liquid-air basis were taken from the ICT *(37).* From other authors, 89 data points were not accepted. As in the case for carbon tetrachloride, the rejected data seemed to define two coherent bands, one clearly above and one clearly below the central band accepted. The accepted group possessed a very good internal consistency with a standard deviation at the mean of 0.03 dyn/cm.

With respect to the water-air system, there are a great many surface tension measurements. For the purposes at hand, we averaged the four sets of linear coefficients provided by Gittens *(27)* for his two sets of data plus those of Teitelbaum *(82)* and Moser *(49).* The resultant linear equation is presented in Table 111.

SURFACE THERMODYNAMIC CONSIDERATIONS

The Gibbs convention regarding the nature of an interface offers a simple physical model, yet one that is sufficiently meaningful to be the basis for precise definitions of terms and equations expressing the thermodynamic properties of capillary systems. According to this model, the two phases in contact remain homogeneous in their properties (such as concentrations) up to the geometric dividing surface that is the interface. This surface of zero thickness is used instead of the real interface of finite thickness. Properties are assigned to the dividing surface such that the energy, composition, and other properties of the total system are conserved. This treatment leads to the definitions employed here for the surface properties. Sometimes surface properties are called surface excess properties, but this terminology is easily confused with ordinary excess properties. Now these assigned properties differ depending upon the exact positioning of the geometric dividing surface. Therefore, the location of the dividing surface is a matter of extreme importance when studying absorption processes.

The systems dealt with in this paper are the simplest ones involving capillary phenomena. In essence, they involve pure liquids in equilibrium with their vapors (no air present) separated by a plane interface. In this connection it is worth noting that actually liquid-air systems differ slightly in their surface properties from the idealized system. Sometimes sufficient information is available to convert measurements for one case to the other case. See ICT *(37).* We will denote by superscript σ those values of the variables that represent surface properties. The application of the Gibbs model, plus the assumption of temperature, concentration, and surface adsorption as the controlling variables, leads to the following intensive properties of the surface (15, *44).*

- $f'' = \sigma = \text{Helmholtz free energy per unit area} = \text{ergs/cm}^2$ $s^{\sigma} = - d\sigma/dT$ = surface entropy per unit area = ergs/ cm 2 $^{\circ} \rm{K}$
- $u^{\sigma} = f^{\sigma} + Ts^{\sigma}$ = total surface energy per unit area = ergs/ $\rm cm^2$
- h^{σ} = surface enthalpy per unit area = ergs/cm²
 $h^{\sigma} = \sigma T(d\sigma/dT)$

When the properties of an entire system are considered, the capital letters of F , S , U , and H are employed.

The surface energy per unit area, u^{σ} , may be viewed as comprising two contributions: one being the work done, σ , and the other the heat requirement *Ts"* necessary to maintain the temperature constant when the area is changed by one unit. This point of view leads to the definition of
 $\lambda^{\sigma} = T s^{\sigma} = - T(d\sigma/dT)$

$$
\lambda^{\sigma} = T s^{\sigma} = - T (d\sigma/dT)
$$

where λ^{σ} is the latent heat of the extension of the surface per unit area. If σ is a linear function of temperature, the surface energy per unit area is constant and $du^{\sigma}/dT = 0$.

DERIVED SURFACE PROPERTIES

By use of the data in Tables I1 and 111, the surface thermodynamic properties were calculated employing the listed thermodynamic relationships. The results are presented in Table IV. In the case of carbon tetrachloride, water, and toluene, the surface tension values were calculated from the linear equations in Table 111.

The results clearly indicate that for one-component liquidair (or vapor) systems that are liquids in normal experience, the surface energy per unit area is remarkably constant over the range from about 0-100°C. Others have made this same finding, but with not the same precision.

In contrast, some authors feel that sometimes surface tension shows nonlinearities in its relationship with temperature. When this assumption is made, such as by Franks and Ives

Table IV. Surface Thermodynamic Properties

 (25) for water-air, the surface energy per unit area for a one-component system is not constant. With two-component systems (like benzene-water), the mathematical treatment illustrated here for one-component systems is not applicable; it is necessary to take into consideration the buildup of sur-
face concentrations, $N \cdot \sigma$, of the two components. For ex-

ample, see Rehbinder *(67).* This point is not always recognized, as is attested by a number of papers on the interfacial tension of hydrocarbon-water systems.

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NOMENCLATURE

- $A =$ surface area, cm²
- N_i^{σ} = surface concentration of *i*th component, g-mol/cm²
- $h^{\sigma} = U^{\sigma}/A$ = enthalpy of the surface per unit area, $dyn/cm = erg/cm²$
- $u^{\sigma} = U^{\sigma}/A =$ total surface energy per unit area, dyn/cm = erg/cm2
- $s^{\sigma} = S^{\sigma}/\tilde{A}$ = entropy of surface formation per unit area, $dyn/cm °K = erg/cm² °K$
- $f^{\sigma} = F^{\sigma}/A =$ Helmholtz free energy of surface formation per unit area, $dyn/cm = erg/cm^2$
- λ^{σ} = latent heat of surface formation per unit area, dyn/cm $=$ erg/cm²
- $\sigma =$ surface tension, dyn/cm = erg/cm²
- $T =$ absolute temperature, K
- $t =$ Celsius temperature, $^{\circ}$ C

H, V, F, and S apply to entire phase, erg

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Critical Reassessment of Viscosities of 11 Common Gases

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Recommended values of the coefficients of viscosity of 11 common gases (He, Ne, Ar, Kr, Xe, N₂, H₂, O₂, CO₂, CH₄, air) are given over the temperature range for which **reliable data exist. A critical reassessment of all available data confirms the recently expressed view that most of the early measurements of high-temperature viscosities are seriously in error (by up to 8% at 1700K). These results have been rejected in favor of more recent data in establishing the values recommended in this paper and estimated to be accurate to 1 .0-1.57&**

The values of the viscosities of even the most common gases have been the subject of some controversy in recent years. Accurate values of this property are most important both from the practical standpoint, in flow and heat exchange problems, and also in theoretical problems where a knowledge of gas viscosities over a wide range of temperature can play an important part in furthering our understanding of the forces between molecules (S, 49). The controversy which has surrounded this property arises from a gross discrepancy between the mutually consistent values of Trautz *(64-76)* and Vasilesco *(80),* obtained during the 1930's and '40's, and the determinations of recent workers, which are not always so mutually consistent. Indications that the earlier results are almost certainly in error have been reported by several workers on the basis of both theoretical *(28,46)* and experimental observations (13, 15, 26). This fact, together with the abundance of viscosity data scattered throughout the literature, makes the need for a critical analysis of the available values very pressing.

The objectives of this survey are threefold: to collect together the many measurements of the viscosities of a number of simple gases; to make a critical assessment of this data in order to decide which data can be accepted as reliable; and using these selected viscosities, to give recommended values over the whole temperature range for which data exist and to give quantitative estimates of their accuracy. The gases studied in this work are the inert gases-helium, neon, argon, krypton, and xenon-the diatomic gases nitrogen, hydrogen, and oxygen and, in addition, carbon dioxide, methane, and air.

DEFINITION AND MEASUREMENT

This survey is concerned with the coefficient of shear viscosity, η , of dilute gases (i.e., gases at low pressures, $\langle 2 \text{ atm} \rangle$. η is defined as the tangential force per unit area required to maintain a unit velocity gradient when a fluid flows past a

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stationary plane surface. Its units are $g \text{ cm}^{-1} \text{ sec}^{-1}$, commonly called the poise; a convenient unit for gas viscosities is the micropoise, μP , 10^{-6} g cm⁻¹ sec⁻¹ or 10^{-7} kg m⁻¹ sec⁻¹. It has been measured using a variety of techniques, the most common of which are the capillary flow method (indicated in the subsequent text by CF) and the oscillating disc (OD) method. Other techniques which have been used to a lesser extent are the rotating cylinder (RC) method and the observation of the retardation from free fall of a body, commonly an oil drop, through the gas.

PROCEDURE

Criteria for Selection **of** Data. Recent measurements of the viscosities of the inert gases by three separate sets of workers using different techniques [Kestin et al. (OD) *(15-17, 33-40),* Guevara et al. (CF) *(22, 26, 21)* and Smith et al. (CF) *(8,* 9, 12, *13, 44)]* have indicated that at high temperatures the hitherto accepted data of Trautz et al. and Vasilesco (both CF) are in error by up to 10% . These serious discrepancies have not yet been satisfactorily explained but may have arisen from inadequate correction of their data and inaccurate temperature measurement *(26).* The data of the three recent workers are not completely consistent with each other, the spread of results being $2.0-2.5\%$. Here we have attempted to estimate "best" values based on these more recent data.

Below room temperature, measurements by Clarke and Smith *(CF)* $(8,9)$ have again suggested errors in the older data of Johnston et al. (OD) *(31,* **32),** but here the discrepancies axe much smaller than those at high temperatures and are not considered significant enough to justify rejection of the earlier work.

The general criteria for accepting data were thus based on the plausible assumption that the recent values for the eleven gases of Kestin et al., Guevara et al., and Smith et al. (with a maximum spread of 2.5%) form a reliable body of data on which to base the recommended values. Where the data of a worker