**Table IV. Solubilities of $CO_2$ and $SF_6$ in $N_2O_4$**

| | $T$, °K | $p$, atm | $f$, atm[a] | $10^3X$ | $10^3K'$ | $10^3K$ |
|---|---|---|---|---|---|---|
| $CO_2$ in $N_2O_4$ | 262.15 | 0.5773 | 0.5746 | 21.03 | 36.43 | 36.60 |
| | 273.15 | 0.1700 | 0.1698 | 5.276 | 31.04 | 31.07 |
| | | 0.3366 | 0.3358 | 10.18 | 30.24 | 30.32 |
| | | | | | | Av 30.70 |
| | 283.20 | 0.3495 | 0.3488 | 8.712 | 24.93 | 24.98 |
| | | 0.6690 | 0.6663 | 16.42 | 24.54 | 24.65 |
| | | | | | | Av 24.82 |
| | 293.15 | 0.1763 | 0.1761 | 3.742 | 21.23 | 21.25 |
| | | 0.3175 | 0.3169 | 6.524 | 20.55 | 20.59 |
| | | 0.6225 | 0.6203 | 12.65 | 20.32 | 20.39 |
| | | | | | | Av 20.74 |
| $SF_6$-$N_2O_4$ | 263.15 | 0.7095 | 0.7005 | 8.179 | 11.53 | 11.68 |
| | | 1.3778 | 1.3439 | 16.48 | 11.96 | 12.26 |
| | | | | | | Av 11.97 |
| | 278.13 | 0.6635 | 0.6570 | 6.427 | 9.687 | 9.782 |
| | | 1.3957 | 1.3667 | 13.96 | 10.00 | 10.214 |
| | | | | | | Av 9.998 |
| | 293.14 | 0.4394 | 0.4370 | 3.643 | 8.291 | 8.336 |
| | | 0.9478 | 0.9365 | 8.013 | 8.454 | 8.556 |
| | | 1.1006 | 1.0854 | 9.346 | 8.492 | 8.611 |
| | | | | | | Av 8.501 |

[a] $f = ZP$ = fugacity; $X$ = mole fraction; $K' = X/P$; $K = X/f$. $Z$ for $CO_2$ has been taken from Hilsenrath et al. (*8*).

The solubilities of $CO_2$ in $N_2O_4$ and CO in UDMH are small enough to permit the use of these gases as pressurants in the low cost boosters. The solubility of $SF_6$ is small in MH but large enough in $N_2O_4$ to permit the use of this gas as an electrophyllic substance.

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# Vapor Pressures and Second Virial Coefficients of Some Five-Membered Heterocyclic Derivatives

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**Vapor pressures and second virial coefficients of furan, thiophene, pyrrole, and some of their substituted derivatives were measured by an isoteniscopic method in the temperature range 60–100°C.**

Knowledge of vapor pressures and virial coefficients is necessary for the study of molecular interactions in systems involving a vapor phase—homogeneous gas phases or heterogeneous liquid-vapor systems. Especially gas-liquid chromatography allows the determination of activity coefficients $\gamma_i$ of volatile solutes in the liquid stationary phase, from the well-known relationship:

$$V_g = \frac{273\ R}{f_i^0 \gamma_i^0 M} \quad (1)$$

where $V_g$ is the specific retention volume of the compound $i$, $f_i^0$ is its vapor fugacity at the column temperature, and $M$ is the molecular weight of the stationary phase.

When helium is used as the carrier gas, the interactions between the vapor of the solute $i$ and this carrier gas can be neglected, and the fugacity $f_i^0$ is related to the vapor pressure $P_i^0$ and to the second virial coefficient $B_{ii}$ by the equation:

$$\ln f_i^0 = \ln P_i^0 + \frac{P_i^0}{RT} (B_{ii} - v_i^0) \quad (2)$$

where $v_i^0$ is the molar volume of the pure liquid compound $i$. The derivation of these equations and the range of validity were discussed previously (*1*, *2*).

The following measurements were performed with the aim of calculating the activity coefficients $\gamma_i$ from chromatographic retention data using Equation 1. Since the values of $P_i^0$ and $B_{ii}$ thus obtained were of more general use, it seemed useful to publish these data independently of any application.

## EXPERIMENTAL

Measurements were made by the isoteniscopic method with the apparatus shown in Figure 1. The flask (A) containing the investigated compound and the null manometer (B) were immersed in a thermostated oil bath. The pressure measurements were made with the external manometer (C). Metallic contacts (m) and an electrovalve (D) permitted regulation of the mercury levels in the null manometer when the pressure in A approached equilibrium.

The investigated compound was introduced in the flask (A) through the Torion valve (E) (Prolabo, Paris, France) with a

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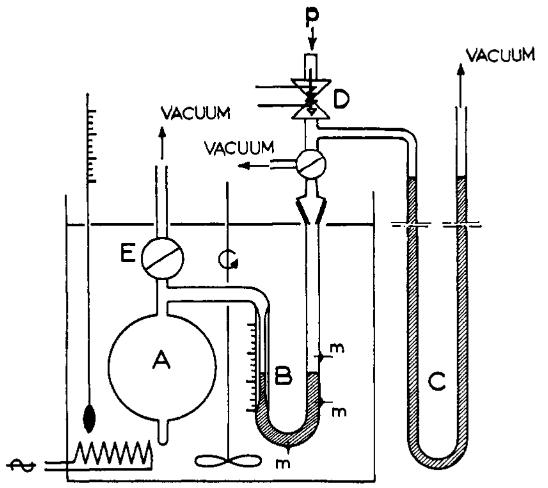

Figure 1. Scheme of apparatus

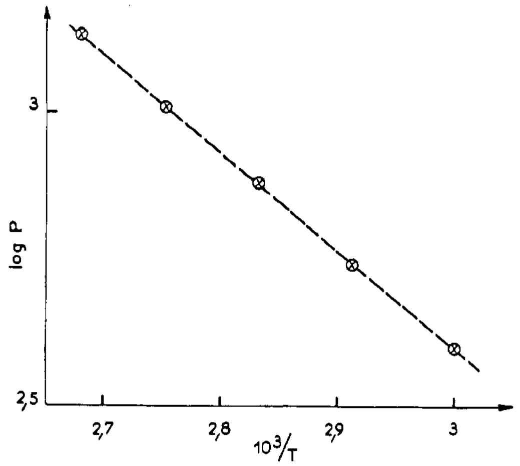

Figure 2. Vapor pressure of benzene, mm Hg

⊗ This work
--- (1)

syringe (Hamilton, Whittier, Calif.) and a small Teflon tube. The syringe and the tube were weighed before and after the operation for the exact amount of liquid introduced. During this step, the bottom of A was cooled in a dry ice bath after which the entire apparatus was evacuated.

The valve (E) was closed and parts A and B were immersed slowly in the oil bath. When equilibrium was reached, the vapor pressure in A was determined from the measured differences $\Delta h_B$ and $\Delta h_C$ in the levels of the two manometers B and C.

$$P_{i(T)} = \Delta h_B + \Delta h_C - P_{\mathrm{Hg}^0(T)} \qquad (3)$$

where $P_{\mathrm{Hg}^0(T)}$ is the vapor pressure of mercury at the oil bath temperature $T$. $\Delta h_B$ and $\Delta h_C$ were measured with a cathetometer with a precision of 0.01 mm; $\Delta h_B$ was quite small if the pressure behind the valve (D) was not too different from $P_i$. The absolute error on the measurement was less than 0.1 mm Hg.

The temperature of the oil bath was controlled within 0.05° C, and the gradient in the zone of the bath where the equipment was placed was smaller than 0.02° C. When the flask (A) contained vapor of the studied compound in equilibrium with the liquid, the measured pressure was $P_i^0$. When A contained only vapor and no liquid, the second virial coefficient $B_{ii}$ could be determined from the measured pressure $P_i$ using the equations:

$$\frac{P_i V}{n_i} = Z_i RT \qquad (4)$$

and

$$B_{ii} = \frac{RT}{P_i}(Z_i - 1) \qquad (5)$$

where $V$ is the volume of the vapor, $n_i$ is the number of moles of compound introduced in the flask, and $Z_i$ is the compressibility coefficient of $i$.

Volume $V$ was measured at 80° C by weighing the system (A + B) with a normal level of mercury in B at 80° C and with part A filled with mercury at the same temperature. We assumed that this volume can be considered constant in the investigated temperature range—i.e., 60–100° C.

The studied derivatives were pure grade compounds (Aldrich Chemical Co.) distilled twice under vacuum before use. Since their gas chromatographic analyses showed only a single peak in each case, the purity of the compounds was at least 99%.

For each compound about 12 measurements were made, first increasing the bath temperature from 60–100° C and then decreasing this temperature in the same range. The validity of the entire procedure was verified by measuring the vapor pressure and second virial coefficient of benzene. The experimental results were in good accordance with the values found in the literature.

## RESULTS

**Vapor Pressure Measurements.** The reproducibility of the measurements was better than 0.5% except for the thiophene brominated derivatives which have a lower thermal stability; therefore, a new freshly distilled sample was used every second or third measurement.

The values of the vapor pressure $P_i^0$ thus obtained were fitted by a least-squares method with the Clausius-Clapeyron equation:

$$\ln P_i^0 = -\frac{\Delta H_i^v}{RT} + \frac{\Delta S_i^v}{R}$$

where $\Delta S_i^v$ and $\Delta H_i^v$ are the standard entropy and apparent enthalpy of vaporization, at temperature $T$.

The experimental vapor pressures of benzene were in ex-

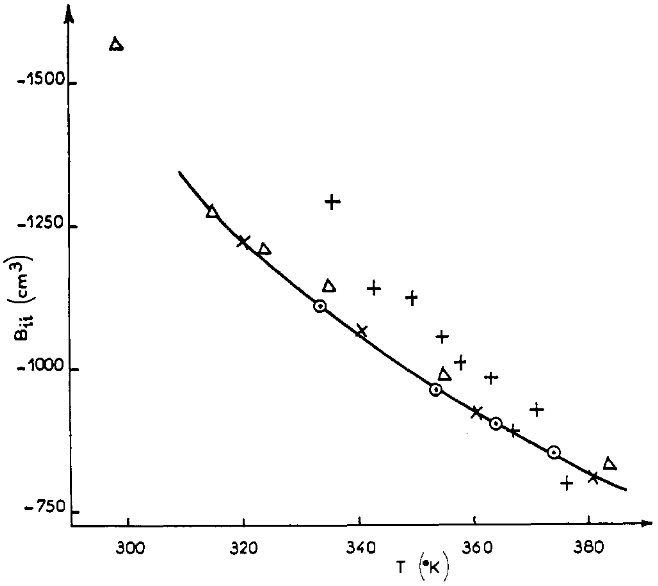

Figure 3. Second virial coefficient of benzene

+ (5) △ (6)
× (4) ⊙ This work

### Table I. Vapor Pressures and Apparent Enthalpy of Vaporization of Some Five-Membered Heterocyclic Derivatives

| | Vapor pressure, mm Hg | | | | | |
|---|---|---|---|---|---|---|
| Compound | 60.3°C | 70.3°C | 80.3°C | 90.3°C | 100.3°C | $-\Delta H^v$ kcal/mol |
| 2-Methylfuran | 646 | 893 | 1213 | 1620$^a$ | 2130$^a$ | 7.36 |
| Tetrahydrothiophene | 97.1 | 144 | 208 | 296 | 412 | 8.93 |
| Thiophene | 337 | 486 | 686 | 951 | 1294$^a$ | 8.31 |
| 2-Methylthiophene | 129 | 190 | 274 | 386 | 535 | 8.79 |
| 3-Methylthiophene | 116 | 172 | 249 | 353 | 490 | 8.89 |
| 2,5-Dimethylthiophene | 55.5 | 84.2 | 125 | 181 | 257 | 9.48 |
| 2-Ethylthiophene | 60.9 | 92.2 | 136 | 197 | 280 | 9.44 |
| 2-Chlorothiophene | 104 | 149 | 210 | 290 | 393 | 8.22 |
| 2,5-Dichlorothiophene | 36.4 | 51.9 | 72.5 | 99.4 | 134 | 8.05 |
| 2-Bromothiophene | 78.1 | 104 | 138 | 179 | 229 | 6.67 |
| 3-Bromothiophene | 56.7 | 76.8 | 102 | 134 | 173 | 6.88 |
| 3,4-Dibromothiophene | 7.1 | 9.9 | 13.6 | 18.5 | 24.5 | 7.64 |
| 2-Iodothiophene | 28.0 | 38.0 | 50.7 | 66.5 | 86 | 6.93 |
| Pyrrole | 62.9 | 97.7 | 148 | 219 | 317 | 10.00 |
| 1-Methylpyrrole | 124 | 184 | 268 | 381 | 533 | 9.01 |
| Benzene | 397 | 556 | 764 | 1031 | 1370 | 7.64 |

$^a$ Extrapolated value.

### Table II. Second Virial Coefficients of Some Five-Membered Heterocyclic Derivatives

| | Second virial coefficient, cm$^3$/mol | | | | |
|---|---|---|---|---|---|
| Compound | 60.3°C | 70.3°C | 80.3°C | 90.3°C | 100.3°C |
| Cyclopentene | −820 | −755 | −710 | −665 | −630 |
| 2,5-Dihydrofuran | −670 | −630 | −595 | −565 | −535 |
| Furan | −645 | −605 | −570 | −535 | −500 |
| 2-Methylfuran | −810 | −760 | −725 | −690 | −670 |
| Tetrahydrothiophene | −910 | −875 | −840 | −760 | −710 |
| Thiophene | −1020 | −970 | −915 | −865 | −820 |
| 2-Methylthiophene | −1700 | −1610 | −1490 | −1390 | −1310 |
| 3-Methylthiophene | −1830 | −1680 | −1550 | −1430 | −1320 |
| 2,5-Dimethylthiophene | −2410 | −2280 | −2160 | −2040 | −1920 |
| 2-Ethylthiophene | −2210 | −2070 | −1970 | −1890 | −1790 |
| 2-Chlorothiophene | −2060 | −1930 | −1830 | −1730 | −1650 |
| Pyrrole | −1270 | −1160 | −1070 | −990 | −880 |
| 1-Methylpyrrole | −1370 | −1200 | −1190 | −1120 | −1050 |
| Benzene | −1110 | −1030 | −960 | −900 | −850 |

cellent agreement (Figure 2) with the values given in the literature (*3*). The vapor pressures and the apparent enthalpy of vaporization of the derivatives studied here are reported in Table I.

**Second Virial Coefficient Measurements.** The small volume of the flask (A) used (about 200 cm$^3$) limited the precision obtained in the determination of $B_{ii}$. Small quantities of the compound must be introduced and weighed. However, the experimental values obtained for benzene were in good agreement (Figure 3) with those published by various authors (*4–6*), and the relative error made in the determination of $B_{ii}$ can be estimated less than ±4%. The results are reported in Table II.

## CONCLUSION

The isoteniscopic method used in this work allowed simple and fast measurements of vapor pressures and virial coefficients. In major cases, where the thermal stability of the studied compounds is sufficient, the relative error on pressure measurements was less than 0.3% and the error on temperature led to a relative error on vapor pressure less than 0.2%. The total relative error on vapor pressure measurements was probably less than 0.5%, in accordance with the reproducibility observed. The reproducibility of the measurements in the $B_{ii}$ determination was only about 4% because of the error on the weight of the small samples investigated, but this precision was sufficient when $B_{ii}$ was used as a corrective factor—i.e., in the activity coefficients calculated from Equation 1.

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