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# Vapor Pressure Determination of Eight Oxygenated Compounds

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**The vapor pressures of two ethers and of six carbonyl compounds were measured in order to enlarge a data base used in developing a group contribution method for the estimation of pure component vapor pressure. An ebulliometer was the central piece of apparatus used in obtaining subatmospheric vapor pressure data while superatmospheric measurements were obtained in a capillary apparatus by observing the meniscus. The compounds included in the study were acetylacetone, allyl phenyl ether, 1,1-diethoxypropane, dimethyl malonate, dimethyl oxalate, isopropenyl acetate, isobutyl acrylate, and methyl isobutyrate. The overall range of temperature measurements extended from 284.9 to 619.6 K. Pressures ranged from 2846 to 3 863 000 Pa. Correlating equations were fit to the data for each compound.**

## Purpose

To enhance the representation of carbonyl and ether compounds in a data base used for the development of a group contribution correlation for vapor pressure, the vapor pressures of eight compounds were measured. The two ethers were 1,1-diethoxypropane and allyl phenyl ether. The carbonyls were acetylacetone, dimethyl malonate, dimethyl oxalate, isobutyl acrylate, isopropenyl acetate, and methyl isobutyrate. The vendors and purities of the compounds are given in Table I.

## Experimental Apparatus and Procedure

***High-Pressure Apparatus.*** The apparatus designed by Kay (*1*, *2*) at Ohio State University as modified by Spencer (*3*) can be used to measure vapor pressures from slightly below the normal boiling point to pressures up to the critical point for thermally stable compounds. As shown in Figure 1, the apparatus consists of a mercury compression block (items 8–10) containing mercury in which is inserted a glass sample tube with a 2.5-mm inner diameter. The pressure on the sample is controlled by valves (items 30–36, 38, 39) regulating the flow of nitrogen gas onto the back leg of the compression block. A 1000 psig capacity Heise gauge monitors the pressure on the sample tube. Spencer (*3*) describes in detail the features of the mercury compression block. The sample temperature is regulated by boiling an organic substance in the heating jacket (item 2). The four organics used as heating media were phenyl ether, bromobenzene, benzophenone, and carbazole. No single compound could be used for the wide range of temperature covered by this work. The temperature is measured by a copper–constantan thermocouple monitored by a Leeds and Northrup millivolt potentiometer. The jacket pressure is controlled by needle valves j (items 25–28) regulating the flow of either nitrogen or helium gas. A closed-end manometer (item 29) monitors the jacket pressure. A vacuum pump evacuated the heating jacket when the needle valves are appropriately positioned. All glassware was cleaned in a solution made by adding Godax Laboratory's Nochromix crystals to concentrated sulfuric acid.

***Summary of High-Pressure Procedure.*** A clean sample tube is filled with 0.1–1.0 cm (as viewed in the sample tube) of organic sample by using a capillary tube as a funnel. The appropriate amount of sample depends on the temperature range to be investigated. The sample is then degassed by using the apparatus shown in Figure 2. The sample is first frozen by inserting the tube in liquid nitrogen. Then the vacuum pump is turned on and the liquid nitrogen is removed from the end of the sample tube, allowing the sample to thaw. As the thawing sample starts to move up the sample tube under vacuum, the valve to the atmosphere is opened and the sample is frozen again. This process is repeated four times or until no air bubbles are seen leaving the thawing sample.

Next the sample tube is filled up with liquid mercury an inch at a time with the aid of a closed-end capillary tube (this controls the rate that mercury falls inside the tube). After filling with mercury the tube is installed on the mercury compression block. The heating jacket and overhead condenser are placed over the sample tube. A nichrome wire (item 4 in Figure 1) located in the heating jacket is given enough heat to create a clear film of condensing organic on the jacket wall to enhance sample tube visibility. A vacuum is imposed on the heating jacket after it has been evacuated and filled with nitrogen gas. If the operating temperature is to exceed 347 °C then helium serves as the inert to prevent oxidation and degradation of the heating medium.

The sample is pressurized with a pressure greater than its expected dew point. After the sample has reached the temperature of the boiling organic (which takes about 5–10 min), the sample pressure is lowered until it has reached its dew point. At the dew point a tiny amount of liquid appears at the corners of the mercury meniscus. The dew point is used instead of the bubble point because the former is less sensitive to the presence of low-boiling impurities than the latter. When at the temperature of interest, the sample's dew point is stable for about 8 min, the potentiometer and Heise gauge readings are taken. The jacket pressure is then raised to achieve a higher temperature and the above step is repeated. Askonas (*4*), Stein (*5*), Jalowka, (*6*), and LeMieux (*7*) all used the same apparatus and give more details on the procedure (*11*).

To calculate the sample vapor pressure the mercury head in the sample tube and in the back section of the mercury compression block are accounted for together with the Heise gauge calibration and the barometric pressure.

According to LeMieux (*7*) the Heise gauge is accurate to ±0.3 psi. Accounting for the Heise gauge calibration brings the total estimated error in calculated vapor pressures to ±0.5 psi.

The Leeds and Northrup millivolt potentiometer can be read to the nearest 0.001 mV which corresponds to approximately 0.02 °C. Accounting for the thermocouple calibration of LeMieux (*7*), the overall error in temperature measurements is about ±0.1 °C.

***Low-Pressure Apparatus.*** Ebulliometers were used to measure subatmospheric vapor pressures. An ebulliometer (Figure 3) is joined with two condensers and a vacuum system. An ebulliometer consists of a sample compartment holding 18–20 mL of sample, and flow channels for saturated vapor to leave the sample compartment and condensate to return to the sample compartment. A cylindrical metal heating element whose voltage is regulated by a variac provides heat. Saturated vapor travels upward and spurts onto the thermowell where it condenses and drops down on its way back to the heating chamber. The primary condenser is cooled by running water. Fiberglass insulation is placed around the sample compartment and on the narrow channel through which saturated vapor

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**Table I. Vendors and Purities of Experimental Compounds**

Fluka Chemical Co.

| compd | $d_4^{20}$ | $n^{20}{}_D$ | purity grade | purity (GC) | bp, °C | mp, °C |
|---|---|---|---|---|---|---|
| acetylacetone | 0.972 | 1.452 | puriss., p.a. | >99.5% | 136–138 | |
| 1,1-diethoxypropane[a] | 0.828 | 1.389 | purum | >97% | 120–123 | |
| dimethyl malonate | 1.153 | 1.413 | purum | ~98% | n.a. | |
| dimethyl oxalate | n.a.[b] | n.a. | purum | >99% | n.a. | 50–53 |
| isobutyl acrylate[c] | 0.88 | 1.415 | purum | >99% | 139 | |
| isopropenyl acetate | 0.920 | 1.401 | purum | >99% | 95–97 | |
| methyl isobutyrate | 0.891 | 1.384 | puriss. | >99% | 91–93 | |

Meaning of Symbols/Abbreviations: Fluka

| | |
|---|---|
| $d_4^{20}$ | density at 20 °C based on density of water at 4 °C |
| $n^{20}{}_D$ | refractive index at 20 °C using the Abbe refractometer |
| GC | composition by peak area percentage, sometimes as dry wt % |
| bp | boiling point determination with Fus-o-Mat; determination of the boiling range according to special methods of ASTM, ACS, Ph. Helv., etc. |
| mp | melting point determination with FP51 (Mettler) or according to Dr. M. Tottoli |

Aldrich Chemical Co.

| compd | $d$ | $n^{20}{}_D$ | purity | bp, °C |
|---|---|---|---|---|
| allyl phenyl ether | 0.978 | 1.5200 | 99% | 192 |

Meaning of Symbols/Abbreviations: Aldrich

| | |
|---|---|
| $d$ | density at 20 ± 5 °C relative to water at 4 °C |
| $n^{20}{}_D$ | index of refraction for the sodium D line at 20 °C |

[a] Values listed for 1,1-diethoxypropane are from the 1984–1985 Fluka Catalog but were not on the label. [b] n.a. = not available. [c] Stabilized by Fluka with 0.005% hydroquinone.

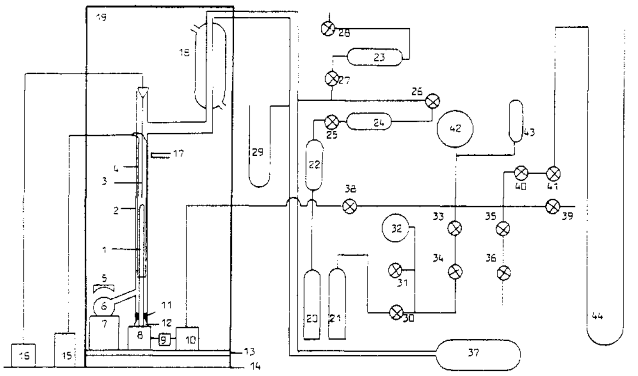

**Figure 1.** Kay apparatus: (1) sample tube; (2) heating jacket; (3) copper constantan thermocouple; (4) nichrome wire; (5) upper heating mantle; (6) side arm boiling flask; (7) lower heating mantle and variac; (8) front mercury leg; (9) compressor block assembly; (10) rear mercury leg; (11) mercury layer; (12) rubber stopper; (13) mercury spill tray; (14) supporting platform; (15) variac for nichrome wire; (16) potentiometer; (17) air stream; (18) water condenser; (19) hood; (20) inert gas tank; (21) nitrogen tank; (22) surge tank; (23) vacuum line pressure adjusting bulb; (24) inert gas pressure adjusting bulb; (25–28) needle valves; (29) closed end manometer; (30) gas line valve; (31) release valve; (32) pressure gauge; (33–34) system inlet valves; (35–36) system exhaust valves; (37) surge tank; (38) compressor inlet valve; (39) dead weight tester valve; (40) pressure check valve; (41) release valve; (42) heise gauge; (43) surge tank; (44) open end manometer.

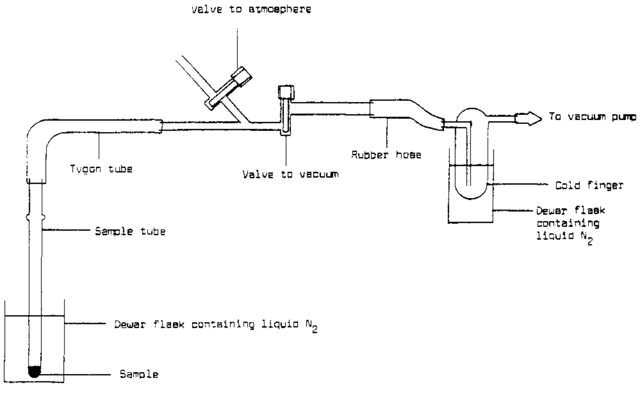

**Figure 2.** The degassing apparatus.

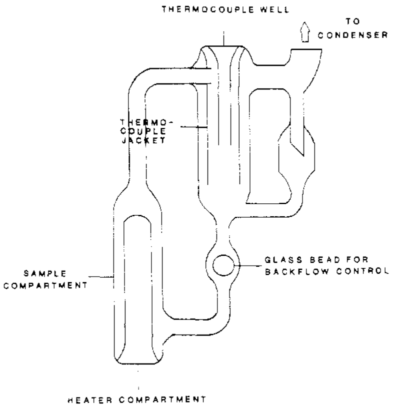

**Figure 3.** Ebulliometer.

flows. Dry ice and acetone were used as the coolant in a specially designed nonflow condenser when isopropenyl acetate, methyl isobutyrate, and 1,1-diethoxypropane were run. At low pressures these compounds' boiling temperatures were too low to allow the use of 13 °C (in December) tap water as the coolant.

An Omega digital thermometer equipped with an iron–constantan thermocouple was used to measure the temperature. This is accurate to approximately ±0.4 °C based on the calibration of Lyons (*8*). A horizontally leveled site glass was used to read the mercury meniscus levels on the 23-in. closed-end manometer used in this work. Pressure readings could be read to the nearest 0.002 psi. Accounting for subjectivity in the alignment of the site glass with the mercury meniscus brings the overall error in the measured vapor pressure to about 0.01 psi.

***Low-Pressure Procedure.*** The sample is placed in an ebulliometer and the condensers are attached. The system is then twice evacuated and filled with nitrogen gas. The system is evacuated a third time and the mercury levels in the manometer are checked after 10 min to ensure the absence of pressure leaks. Then the heating element is turned on and increased at 10-min intervals until steady boiling is achieved. Steady boiling consists of a rapid and even flow of saturated vapor onto the thermowell from the sample compartment.

**Table II. Experimental Temperature/Pressure Ranges and the Normal Boiling Points**

| | $T_{\min}$, K | $P_{\min}$, MPa | $T_{\max}$, K | $P_{\max}$, MPa | NBP[a] | total no. of data points |
|---|---|---|---|---|---|---|
| acetylacetone | 323.9 | 0.004 440 | 596.3 | 2.387 | 415.1 | 78 |
| allyl phenyl ether | 376.3 | 0.005 946 | 478.2 | 0.138 | 462.9 | 24 |
| 1,1-diethoxypropane | 306.0 | 0.002 846 | 427.1 | 0.302 | 391.3 | 20 |
| dimethyl malonate | 374.1 | 0.006 066 | 619.6 | 3.863 | 452.5 | 29 |
| dimethyl oxalate | 347.0 | 0.003 086 | 528.5 | 0.875 | 437.6 | 23 |
| isobutyl acrylate | 321.2 | 0.003 400 | 489.8 | 0.622 | 410.1 | 19 |
| isopropenyl acetate | 301.5 | 0.006 346 | 532.3 | 3.032 | 370.0 | 44 |
| methyl isobutyrate | 284.9 | 0.003 400 | 467.5 | 1.151 | 366.3 | 21 |

[a] Normal boiling point (NBP) interpolated from eq 1 or 2 by using Newton–Raphson root-solving algorithm. [b] The acetylacetone data includes that of Stein (*5*).

**Table III. Vapor Pressure Data of Acetylacetone**

| temp, K | press., Pa | temp, K | press., Pa |
|---|---|---|---|
| 399.3 | 0.6881D+05[a] | 521.3 | 0.8336D+06 |
| 402.8 | 0.7722D+05 | 521.8 | 0.8195D+06 |
| 406.5 | 0.8343D+05 | 524.1 | 0.8743D+06 |
| 409.6 | 0.9308D+05 | 524.8 | 0.8681D+06 |
| 412.8 | 0.9859D+05 | 528.8 | 0.9186D+06 |
| 415.2 | 0.1072D+06 | 532.0 | 0.9575D+06 |
| 418.0 | 0.1129D+06 | 534.7 | 0.1006D+07 |
| 420.7 | 0.1217D+06 | 538.7 | 0.1066D+07 |
| 423.0 | 0.1290D+06 | 542.8 | 0.1131D+07 |
| 425.1 | 0.1355D+06 | 547.2 | 0.1197D+07 |
| 428.7 | 0.1462D+06 | 551.6 | 0.1272D+07 |
| 434.8 | 0.1679D+06 | 555.6 | 0.1353D+07 |
| 439.0 | 0.1854D+06 | 558.9 | 0.1420D+07 |
| 444.6 | 0.2063D+06 | 562.5 | 0.1495D+07 |
| 449.7 | 0.2315D+06 | 565.6 | 0.1553D+07 |
| 453.9 | 0.2506D+06 | 567.2 | 0.1576D+07 |
| 459.1 | 0.2790D+06 | 568.8 | 0.1622D+07 |
| 462.7 | 0.2991D+06 | 572.0 | 0.1671D+07 |
| 466.4 | 0.3232D+06 | 572.1 | 0.1696D+07 |
| 470.1 | 0.3463D+06 | 574.2 | 0.1753D+07 |
| 473.6 | 0.3677D+06 | 575.2 | 0.1773D+07 |
| 477.4 | 0.3967D+06 | 578.0 | 0.1846D+07 |
| 481.0 | 0.4225D+06 | 578.7 | 0.1851D+07 |
| 484.1 | 0.4463D+06 | 582.2 | 0.1930D+07 |
| 486.8 | 0.4678D+06 | 586.1 | 0.2041D+07 |
| 488.3 | 0.4762D+06 | 591.6 | 0.2215D+07 |
| 490.3 | 0.4980D+06 | 596.3 | 0.2387D+07 |
| 493.9 | 0.5285D+06 | | |
| 497.0 | 0.5570D+06 | 323.9 | 0.4440D+04 |
| 497.0 | 0.5307D+06 | 346.9 | 0.1187D+05 |
| 501.2 | 0.5963D+06 | 357.7 | 0.1779D+05 |
| 504.1 | 0.6143D+06 | 365.9 | 0.2426D+05 |
| 505.1 | 0.6412D+06 | 373.5 | 0.3120D+05 |
| 508.5 | 0.6798D+06 | 381.5 | 0.4004D+05 |
| 509.1 | 0.6658D+06 | 384.5 | 0.4408D+05 |
| 512.3 | 0.7205D+06 | 387.9 | 0.4881D+05 |
| 513.8 | 0.7221D+06 | 393.5 | 0.5738D+05 |
| 515.6 | 0.7598D+06 | 397.7 | 0.6499D+05 |
| 517.8 | 0.7745D+06 | 403.2 | 0.7523D+05 |
| 518.5 | 0.7977D+06 | | |

[a] $x$D+0$n$ ≡ $x \times 10^n$.

**Table IV. Vapor Pressure Data of Allyl Phenyl Ether**

| temp, K | press., Pa | temp, K | press., Pa |
|---|---|---|---|
| 376.3 | 0.5946D+04[a] | 435.7 | 0.4779D+05 |
| 379.7 | 0.6593D+04 | 440.2 | 0.5448D+05 |
| 385.3 | 0.8266D+04 | 443.9 | 0.6042D+05 |
| 391.8 | 0.1071D+05 | 447.4 | 0.6579D+05 |
| 397.4 | 0.1331D+05 | 447.5 | 0.6653D+05 |
| 396.7 | 0.1309D+05 | 449.3 | 0.6907D+05 |
| 396.9 | 0.1320D+05 | 451.2 | 0.7327D+05 |
| 405.0 | 0.1843D+05 | 452.2 | 0.7427D+05 |
| 409.2 | 0.2065D+05 | 460.9 | 0.9724D+05 |
| 419.3 | 0.2895D+05 | 465.9 | 0.1081D+06 |
| 425.3 | 0.3496D+05 | 472.7 | 0.1254D+06 |
| 432.2 | 0.4294D+05 | 478.2 | 0.1384D+06 |

[a] $x$D+0$n$ ≡ $x \times 10^n$.

**Table V. Vapor Pressure Data of 1,1-Diethoxypropane**

| temp, K | press., Pa | temp, K | press., Pa |
|---|---|---|---|
| 306.0 | 0.2846D+04[a] | 379.1 | 0.6004D+05 |
| 319.4 | 0.5686D+04 | 386.0 | 0.7560D+05 |
| 329.6 | 0.9146D+04 | 391.9 | 0.9962D+05 |
| 338.2 | 0.1342D+05 | 398.6 | 0.1252D+06 |
| 345.3 | 0.1789D+05 | 403.6 | 0.1511D+06 |
| 351.7 | 0.2300D+05 | 408.5 | 0.1836D+06 |
| 358.0 | 0.2911D+05 | 413.5 | 0.2111D+06 |
| 364.3 | 0.3644D+05 | 418.2 | 0.2335D+06 |
| 369.1 | 0.4317D+05 | 423.9 | 0.2796D+06 |
| 374.1 | 0.5074D+05 | 427.1 | 0.3021D+06 |

[a] $x$D+0$n$ ≡ $x \times 10^n$.

**Table VI. Vapor Pressure Data of Dimethyl Malonate**

| temp, K | press., Pa | temp, K | press., Pa |
|---|---|---|---|
| 374.1 | 0.6066D+04[a] | 487.4 | 0.2688D+06 |
| 384.8 | 0.9566D+04 | 500.1 | 0.3542D+06 |
| 393.4 | 0.1376D+05 | 510.2 | 0.4324D+06 |
| 403.7 | 0.2033D+05 | 520.1 | 0.5396D+06 |
| 412.5 | 0.2809D+05 | 530.3 | 0.6583D+06 |
| 419.1 | 0.3523D+05 | 536.5 | 0.8374D+06 |
| 425.2 | 0.4296D+05 | 547.7 | 0.1053D+07 |
| 430.2 | 0.5048D+05 | 558.7 | 0.1307D+07 |
| 433.5 | 0.5600D+05 | 569.1 | 0.1533D+07 |
| 436.9 | 0.6209D+05 | 583.4 | 0.2018D+07 |
| 439.4 | 0.6715D+05 | 596.7 | 0.2517D+07 |
| 441.0 | 0.7027D+05 | 605.2 | 0.2808D+07 |
| 443.2 | 0.7475D+05 | 616.1 | 0.3492D+07 |
| 465.0 | 0.1554D+06 | 619.6 | 0.3863D+07 |
| 476.0 | 0.2042D+06 | | |

[a] $x$D+0$n$ ≡ $x \times 10^n$.

**Table VII. Vapor Pressure Data of Dimethyl Oxalate**

| temp, K | press., Pa | temp, K | press., Pa |
|---|---|---|---|
| 347.0 | 0.3086D+04[a] | 423.2 | 0.6743D+05 |
| 356.9 | 0.5033D+04 | 427.1 | 0.7565D+05 |
| 366.4 | 0.7886D+04 | 443.5 | 0.1233D+06 |
| 370.1 | 0.9086D+04 | 457.9 | 0.1742D+06 |
| 378.3 | 0.1303D+05 | 465.3 | 0.2183D+06 |
| 390.0 | 0.2107D+05 | 473.8 | 0.2673D+06 |
| 398.3 | 0.2875D+05 | 484.8 | 0.3747D+06 |
| 404.0 | 0.3540D+05 | 492.7 | 0.4387D+06 |
| 409.4 | 0.4264D+05 | 502.5 | 0.5234D+06 |
| 414.2 | 0.5017D+05 | 513.0 | 0.6268D+06 |
| 417.1 | 0.5560D+05 | 528.5 | 0.8753D+06 |
| 420.6 | 0.6229D+05 | | |

[a] $x$D+0$n$ ≡ $x \times 10^n$.

After steady boiling has been achieved at a given pressure, the pressure and variac settings are increased slightly for another measurement. Ten to twenty minutes are required for the establishment of steady boiling at a given pressure.

## Analysis of Experimental Results

Table II lists the experimental temperature and pressure ranges, the total number of data points, and the interpolated normal boiling point of each of the compounds. The vapor pressure data appear in Tables III–X with pressure in pascals and temperature in kelvin.

**Table VIII. Vapor Pressure Data of Isobutyl Acrylate**

| temp, K | press., Pa | temp, K | press., Pa |
|---|---|---|---|
| 321.2 | 0.3400D+04[a] | 393.8 | 0.6208D+05 |
| 332.9 | 0.5966D+04 | 396.6 | 0.6764D+05 |
| 343.3 | 0.9719D+04 | 398.4 | 0.7150D+05 |
| 350.5 | 0.1321D+05 | 400.2 | 0.7509D+05 |
| 361.7 | 0.2055D+05 | 440.1 | 0.2225D+06 |
| 370.5 | 0.2848D+05 | 457.0 | 0.3219D+06 |
| 376.7 | 0.3542D+05 | 469.2 | 0.4309D+06 |
| 382.2 | 0.4259D+05 | 481.1 | 0.5438D+06 |
| 385.8 | 0.4809D+05 | 489.8 | 0.6223D+06 |
| 390.5 | 0.5588D+05 | | |

[a] $x$D+0$n \equiv x \times 10^n$.

**Table IX. Vapor Pressure Data of Isopropenyl Acetate**

| temp, K | press., Pa | temp, K | press., Pa |
|---|---|---|---|
| 301.5 | 0.6346D+04[a] | 423.0 | 0.3930D+06 |
| 308.0 | 0.8839D+04 | 423.7 | 0.4022D+06 |
| 314.3 | 0.1197D+05 | 427.9 | 0.4546D+06 |
| 321.4 | 0.1661D+05 | 429.6 | 0.4495D+06 |
| 327.7 | 0.2176D+05 | 436.9 | 0.5217D+06 |
| 334.4 | 0.2872D+05 | 443.8 | 0.6179D+06 |
| 339.7 | 0.3534D+05 | 447.4 | 0.6366D+06 |
| 344.2 | 0.4180D+05 | 453.6 | 0.7378D+06 |
| 349.3 | 0.5045D+05 | 464.6 | 0.9086D+06 |
| 352.3 | 0.5581D+05 | 467.8 | 0.9931D+06 |
| 356.9 | 0.6562D+05 | 478.5 | 0.1182D+07 |
| 361.3 | 0.7554D+05 | 481.0 | 0.1269D+07 |
| 379.4 | 0.1240D+06 | 491.4 | 0.1521D+07 |
| 383.6 | 0.1497D+06 | 492.3 | 0.1559D+07 |
| 388.1 | 0.1722D+06 | 500.2 | 0.1747D+07 |
| 389.7 | 0.1767D+06 | 504.6 | 0.1917D+07 |
| 394.0 | 0.1914D+06 | 510.0 | 0.2056D+07 |
| 398.6 | 0.2289D+06 | 514.2 | 0.2219D+07 |
| 403.3 | 0.2662D+06 | 520.1 | 0.2435D+07 |
| 409.5 | 0.3113D+06 | 525.0 | 0.2654D+07 |
| 413.9 | 0.3506D+06 | 531.4 | 0.2858D+07 |
| 419.1 | 0.3886D+06 | 532.3 | 0.3032D+07 |

[a] $x$D+0$n \equiv x \times 10^n$.

**Table X. Vapor Pressure Data of Methyl Isobutyrate**

| temp, K | press., Pa | temp, K | press., Pa |
|---|---|---|---|
| 284.9 | 0.3400D+04[a] | 352.4 | 0.6715D+05 |
| 296.8 | 0.6419D+04 | 355.9 | 0.7537D+05 |
| 304.9 | 0.9746D+04 | 389.0 | 0.2308D+06 |
| 312.3 | 0.1374D+05 | 398.5 | 0.2777D+06 |
| 317.0 | 0.1702D+05 | 408.2 | 0.3484D+06 |
| 325.4 | 0.2432D+05 | 419.7 | 0.4821D+06 |
| 332.2 | 0.3207D+05 | 429.1 | 0.5413D+06 |
| 336.8 | 0.3821D+05 | 442.0 | 0.7085D+06 |
| 341.5 | 0.4583D+05 | 455.0 | 0.9098D+06 |
| 346.3 | 0.5440D+05 | 467.5 | 0.1151D+07 |
| 349.2 | 0.6028D+05 | | |

[a] $x$D+0$n \equiv x \times 10^n$.

The data for acetylacetone measured on the Kay apparatus in Table III are those of Stein (*5*) and agree well with the author's low-pressure data.

Little high-pressure data were obtained for allyl phenyl ether because it began polymerizing even with hydroquinone added to the sample.

For 1,1-diethoxypropane little acceptable high-pressure data were obtained. Although data at higher temperatures and pressures than are shown in Table V were taken, they were not valid either because of sample decomposition or due to the presence of air. It appears that even the high-pressure data might indicate the presence of air since they fall above a straight line drawn through the low-pressure data alone.

The low- and high-pressure data for dimethyl malonate and dimethyl oxalate agree very well. These compounds did not decompose or polymerize.

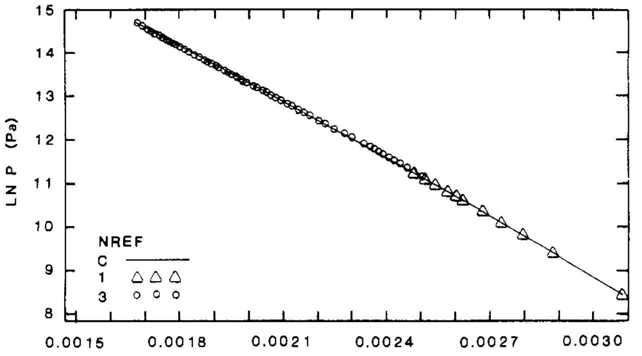

**Figure 4.** Vapor pressure data of acetylacetone.

**Table XI. Error Statistics for Equation Fits of Experimental Data**

| | percent errors | | | |
|---|---|---|---|---|
| | mean | bias | min | max |
| acetylacetone | 2.19 | 1.39 | 0.015 | 6.00 |
| allyl phenyl ether | 1.94 | 2.13 | 0.084 | 10.08 |
| 1,1-diethoxypropane | 4.48 | 4.11 | 0.016 | 12.56 |
| dimethyl malonate | 2.46 | 2.14 | 0.013 | 8.04 |
| dimethyl oxalate | 3.80 | 2.73 | 0.218 | 11.21 |
| isobutyl acrylate | 3.08 | 3.88 | 0.096 | 14.3 |
| isopropenyl acetate | 3.22 | 2.69 | 0.014 | 9.90 |
| methyl isobutyrate | 4.13 | 4.29 | 0.275 | 15.84 |

Isobutyl acrylate (containing hydroquinone in addition to that added by the manufacturer) began polymerizing after the fifth high-pressure datum point.

Isopropenyl acetate's low- and high-pressure data agree well. However, it is believed that near an absolute temperature of 421 K this compound polymerized to a slightly heavier substance. The data above this temperature lie slightly below a straight line drawn through the data from low pressures up to a pressure of 0.4 MPa. The same phenomenon occurred when hydroquinone was added to the sample.

The addition of hydroquinone is not expected to affect the vapor pressure to any significant extent as a very small amount was added and the expected lowering of the vapor pressure would be within the experimental error.

For each chemical, a plot of ln ($P$) vs ($1/T$) was made and best overall fit to the data was determined using either eq 1 or 2. Figure 4 shows a sample plot for acetylacetone with the

$$\ln(P) = A + B/T + C(\ln T) + DT^E \qquad (1)$$

$$\ln(P) = A + B/T \qquad (2)$$

fit shown by the solid line. A SAS routine for nonlinear Levenberg–Marquardt regression was used to determine the coefficients in the equations. In fitting the data to eq 1, the value of $E$ was chosen first (1, 2, or 6) and the remaining four coefficients were determined by the SAS routine. The SAS-determined coefficients of eq 1 were compared with the coefficients determined by a constrained fitting routine which implements certain constraints in selecting the values of the $A$, $B$, $C$, and $D$ coefficients. One of the constraints is that the equation is forced to pass through a given point, usually the critical point. If this is not available the highest experimental point may be used. For acetylacetone, 1,1-diethoxypropane, isopropenyl acetate, and methyl isobutyrate eq 1 fit the data best by causing the equation to pass through the highest experimental temperature/pressure point.

Dimethyl malonate and dimethyl oxalate were best fit by eq 2. The best fit for dimethyl malonate was obtained by omitting the highest temperature/pressure point from the regression. Likewise, the best fit for dimethyl oxalate was obtained by

Table XII. Values of the Coefficients of Regression Eq 1

| | $A$ | $B$ | $C$ | $D$ | $E$ |
|---|---|---|---|---|---|
| acetylacetone | 129.02 | −8624.0 | −17.212 | 0.016971 | 1 |
| allyl phenyl ether | 369.18 | −24.263 | −50.003 | 1.6826E−16[a] | 6 |
| 1,1-diethoxypropane | 136.88 | −9243.2 | −17.613 | 2.2268E−05 | 2 |
| dimethyl malonate | 24.810 | −6011.1 | 0 | 0 | 0 |
| dimethyl oxalate | 24.641 | −5738.6 | 0 | 0 | 0 |
| isobutyl acrylate | 185.04 | −13.284 | −23.528 | 9.0821E−17 | 6 |
| isopropenyl acetate | 76.599 | −7049.1 | −7.7919 | 2.1514E−17 | 6 |
| methyl isobutyrate | 83.597 | −7106.2 | −8.9443 | 5.4205E−17 | 6 |

[a] $x\text{E}{-n} \equiv x \times 10^{-n}$.

Table XIII. Comparison of Normal Boiling Point (K) Values

| compound | expt | vendor | CRC |
|---|---|---|---|
| acetylacetone | 415.1<br>414.3[a] | 409.15–411.15 (Fluka)<br>413.55[b] (Aldrich) | n.a.[c] |
| allyl phenyl ether | 462.9 | 465.15 | 464.85 |
| 1,1-diethoxypropane | 391.3 | 393.15–396.15 | n.a. |
| dimethyl malonate | 452.5 | n.a. | 454.55 |
| dimethyl oxalate | 437.6 | n.a. | 437.65 |
| isobutyl acrylate | 410.1 | 412.15 | 405.15 |
| isopropenyl acetate | 370.0 | 368.15–370.15 | n.a. |
| methyl isobutyrate | 366.3 | 364.15–366.15 | 365.15 |

[a] Obtained from the Newton–Raphson root-solving algorithm using *only* the data of Stein. $A$, $B$, $C$, $D$, $E$ coefficients were fit uniquely to Stein's data: $A = 98.350$, $B = -8785.2$, $C = -10.902$, $D = 1.6286\text{E}{-17}$, $E = 6$. [b] The data of Stein (*5*) were obtained with acetylacetone from Aldrich which was 99+% pure and had the following characteristics (in addition to the NBP noted above): $d = 0.975$; $n^{20}{}_{\text{D}} = 1.4510$. See Table I for meaning of $d$ and $n^{20}{}_{\text{D}}$. [c] n.a. = not available.

omitting the three highest temperature/pressure data points from the regression.

The best fits for allyl phenyl ether and isobutyl acrylate were by eq 1 using the SAS (unconstrained) nonlinear regression and by omitting the two highest temperature/pressure points from the regressions. Table XI shows the percent error statistics of the equation fits using all of the experimental data. Table XII shows the values of the coefficients of eq 1 or 2 for each compound.

## Comparison of Experimental and Literature Normal Boiling Points

The *CRC Handbook of Chemistry and Physics* (*9*) lists normal boiling point values or boiling ranges for five of the compounds studied. The CRC obtained these values from the *Beilstein Handbook*. Referring to Table XIII the "experimental" normal boiling point for allyl phenyl ether (obtained by applying the Newton–Raphson algorithm to the eq 1 fit of the data) is 2 deg below the CRC value and 2.2 K below the Aldrich value. For 1,1-diethoxypropane the experimental value is 1.8 K below the lower end of the range indicated in the Fluka catalog. Dimethyl malonate's experimental value is 2 deg below that given in the *CRC Handbook*. The experimental and CRC normal boiling point values for dimethyl oxalate are in excellent agreement. The experimental value for isobutyl acrylate lies between the Fluka and the CRC values but is closer to the Fluka value of 412.15 K than to the CRC value of 405.15 K. For isopropenyl acetate the experimental value agrees well with the upper end of the range given by Fluka. Methyl isobutyrate's experimental value of 366.3 K is less than 0.2 K above the upper limit of the range indicated by Fluka and is 0.85 K above the CRC value.

The experimental value of 415.1 K for acetylacetone is 4 deg above the Fluka specified value and 1.55 K above the Aldrich value (Stein used the material obtained from Aldrich; the author used the Fluka material). Weiss (*10*) also gives a normal boiling point of 413.55 K for this compound. Linearly interpolating on a plot on ln ($P$) vs $1/T$ between the two data points of Stein (*5*) closest to the normal boiling point (412.8 K, 98.59 kPa; 415.2 K, 107.2 kPa) one obtains a value of 414.4 K for the normal boiling point. Thus the data of Stein deviate less than a degree with the Weiss (*10*) and Aldrich values for the normal boiling point of acetylacetone. This comparison using only the two data points of Stein was done because of the different purities of the acetylacetone samples used for the high- and low-pressure measurements.

By fitting Stein's data (without the author's data) to eq 1 and apolying the Newton–Raphson routine to determine a normal boiling point, one obtains 414.3 K as shown in Table XIII.

## Comparison of Experimental and Literature Subatmospheric Vapor Pressures

The CRC lists a vapor pressure of 746 mmHg at 139 °C for acetylacetone. From the eq 1 fit of the acetylacetone data of Stein and of the author, the calculated pressure is 704.3 mmHg at this temperature. The experimental value is 5.6% less than the CRC value.

Similarly, for 1,1-diethoxypropane the CRC gives a vapor pressure of 744 mmHg at 122.8 °C. The experimental vapor pressure from the eq 1 fit of the data is 884.9 mmHg, which is 18.9% above the CRC value. The CRC source for these subatmospheric vapor pressures is the Beilstein Handbook.

Finally, for isopropenyl acetate the CRC gives a boiling range of 92–94 °C at a pressure of 732 mmHg. Applying the Newton–Raphson root-solving algorithm to the eq 1 fit of the isopropenyl acetate data yields a boiling temperature of 95.65 °C at the pressure of 732 mmHg. Thus the experimental temperature is 1.65 deg above the upper limit of the temperature range given in the *CRC Handbook*.

As much of the data available in the literature for comparison are quite old, the analyses indicate that the data taken appear to be accurate with purity and apparatus limitations.

**Registry No.** Acetylacetone, 123-54-6; allyl phenyl ether, 1746-13-0; 1,1-diethoxypropane, 4744-08-5; dimethyl malonate, 108-59-8; dimethyl oxalate, 553-90-2; isobutyl acrylate, 106-63-8; isopropenyl acetate, 108-22-5; methyl isobutyrate, 547-63-7.

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