

# Physical Properties of Hydrocarbons

## PART 32—Cyclic Ethers

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THE MOST IMPORTANT cyclic ethers are the furan compounds. Furfural is manufactured by treating pentosan with sulfuric acid and steam stripping out the furfural as it is formed. The sources of pentosan are such agricultural products as corncobs, oat hulls, and bagasse. Furfural is used to produce furan and tetrahydrofuran (THF). These products are used as organic intermediates, extraction solvents, polymer solvents, and in polyurethan applications.

Dioxane is produced by heating ethylene glycol in the presence of dehydration catalysts. It finds wide use as a solvent.

**Critical Properties and Vapor Pressure.** Kobe and co-workers have measured the critical properties of furan, THF, and dioxane.<sup>1</sup> The critical temperature and pressure of furfural was estimated by the method of Riedel.<sup>2</sup> When compared with the experimental data on the other three compounds, the method gave an error of about 10° C on the critical temperature and 30-40 psi on the critical pressure. Lydersen's method<sup>2</sup> was used to calculate the critical density, with a probable error of about 0.005 grams/milliliter.

The vapor pressure up to the boiling point is reported in the literature for all four compounds.<sup>3,4,5,6,7</sup> Vapor pressure data up to the critical point are available for furan,<sup>1</sup> THF,<sup>1</sup> and dioxane.<sup>1,8</sup> The method described in previous articles was used to calculate the high temperature vapor pressure of furfural.<sup>9</sup>

Graph 32-2 shows the vapor pressure of dioxane-water solutions.<sup>10</sup>

**Heat of Vaporization.** The heat of vaporization of THF at the boiling point was calculated by the method of Riedel, with a probable error of 1-2 percent.<sup>2</sup> Experimental data at the boiling point are available for furan,<sup>4,11</sup> dioxane,<sup>8,12</sup> and furfural.<sup>13</sup> The data were extended to the critical point by Kharbanda's nomograph of the Watson equation.<sup>14</sup>

**Heat Capacity.** Only the vapor heat capacity of furan has been measured experimentally.<sup>4</sup> The heat capacities of the other three compounds have been estimated,<sup>15</sup> with a probable error of about 5 percent.

Guthrie has measured the liquid heat capacity of furan from -82° C to 26° C.<sup>4</sup> The room temperature values have been determined for dioxane<sup>12,16</sup> and furfural.<sup>13</sup> The room temperature heat capacity of THF was estimated by the additive method proposed by Johnson and Huang.<sup>2</sup> The heat capacities over the 0° to 200° C temperature range were estimated by the method used in previous articles.

**Density.** The room temperature densities<sup>4,6,7,12</sup> have been extended by the method of Lydersen and co-workers to the critical point.<sup>2</sup> The error is probably 1 percent or

TABLE 32-1—Physical Properties of Cyclic Ethers

Compound	Synonym	Boiling Point, °C	Freezing Point, °C	Molecular Weight	Critical Properties		
					T <sub>c</sub> , °C	P <sub>c</sub> , PSIA	d <sub>c</sub> , g/ml
Furan.....	Furfuran	31.4	-85.7	68.07	214	772	0.312
Tetrahydrofuran...	THF	65.5	-65	72.10	268	753	0.322
Dioxane.....	1,4-dioxane	101.4	11.8	88.10	315	755	0.370
Furfural.....	2-furaldehyde	161.7	-38.7	96.08	387*	730*	0.357*

\* Estimated.



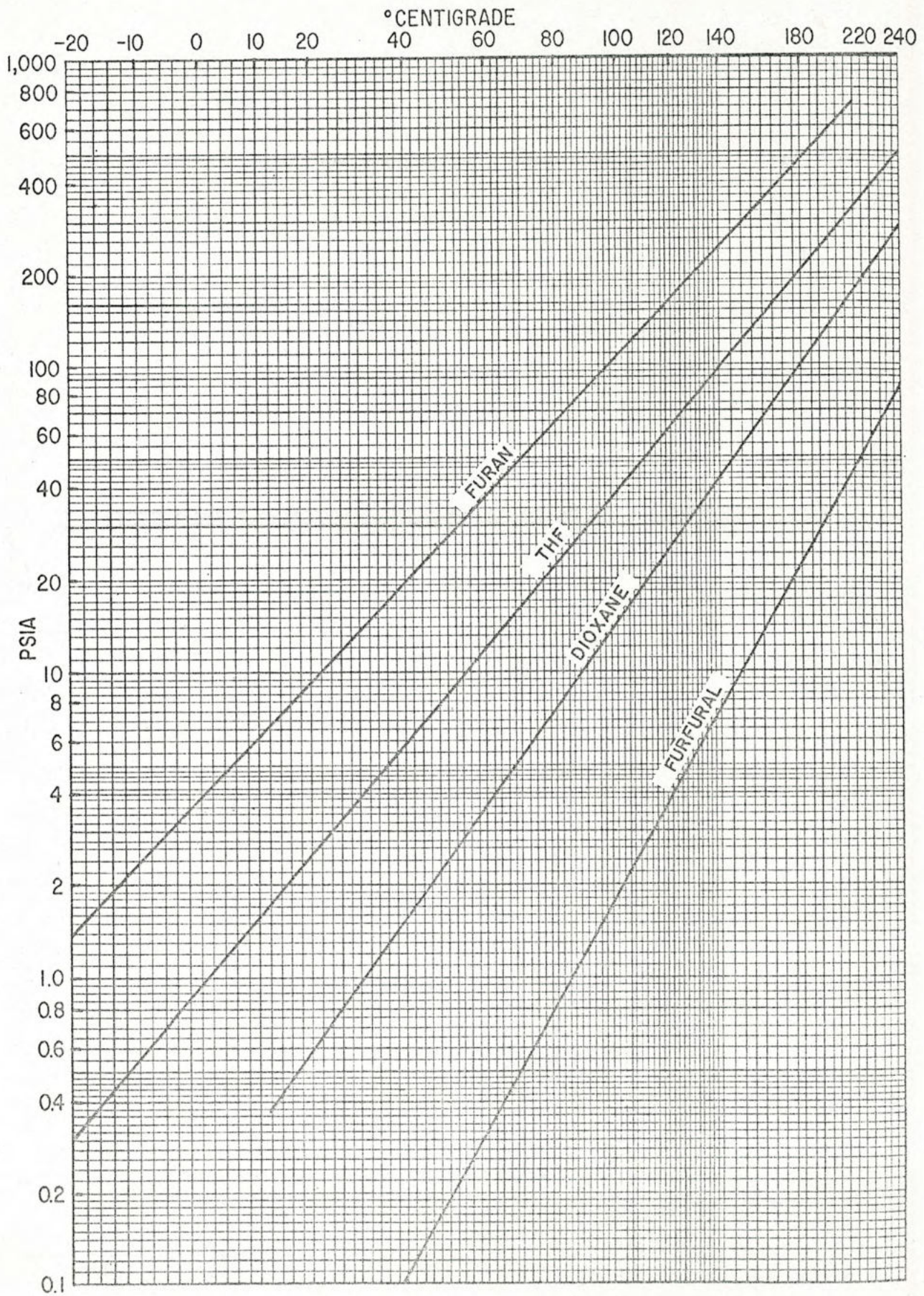


Fig. 32-1—Gives vapor pressures of cyclic ethers from -20° C to +240° C.



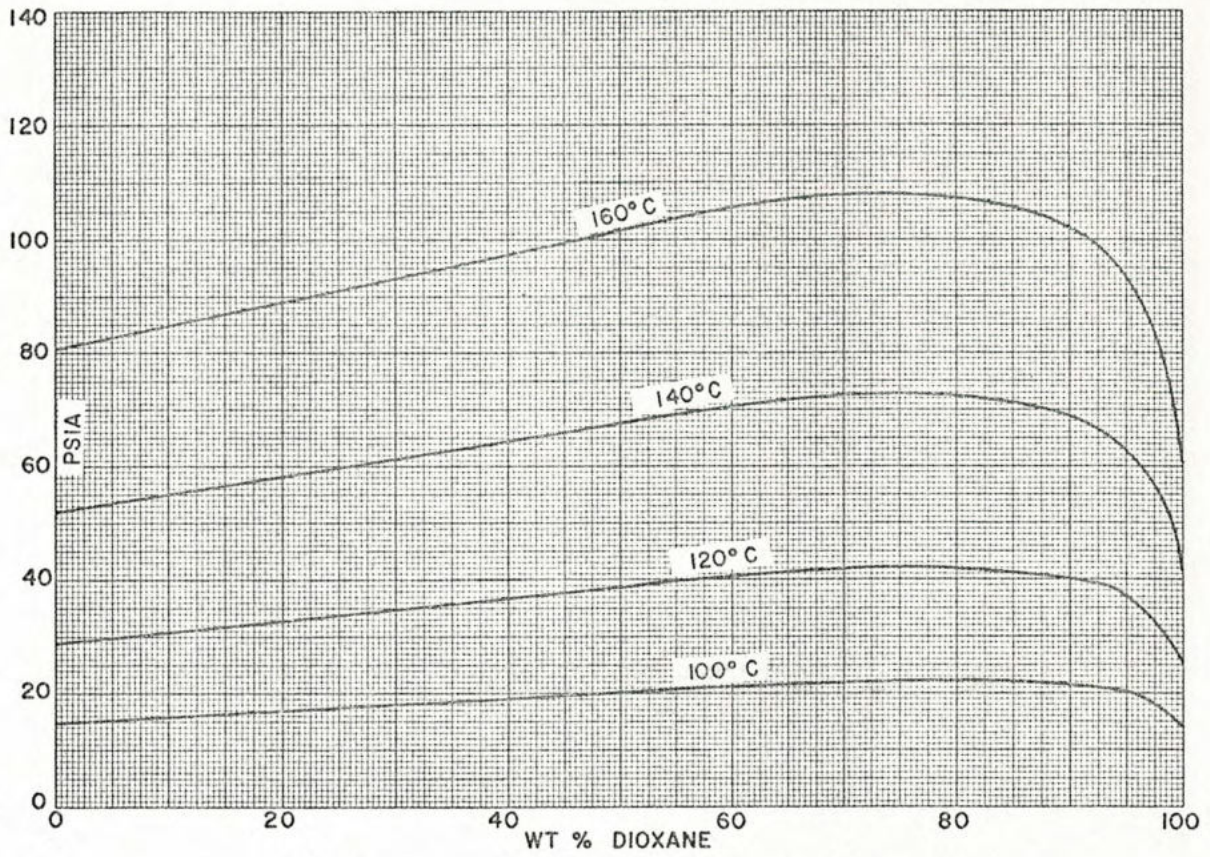


Fig. 32-2—Gives vapor pressure for dioxane-water solutions.

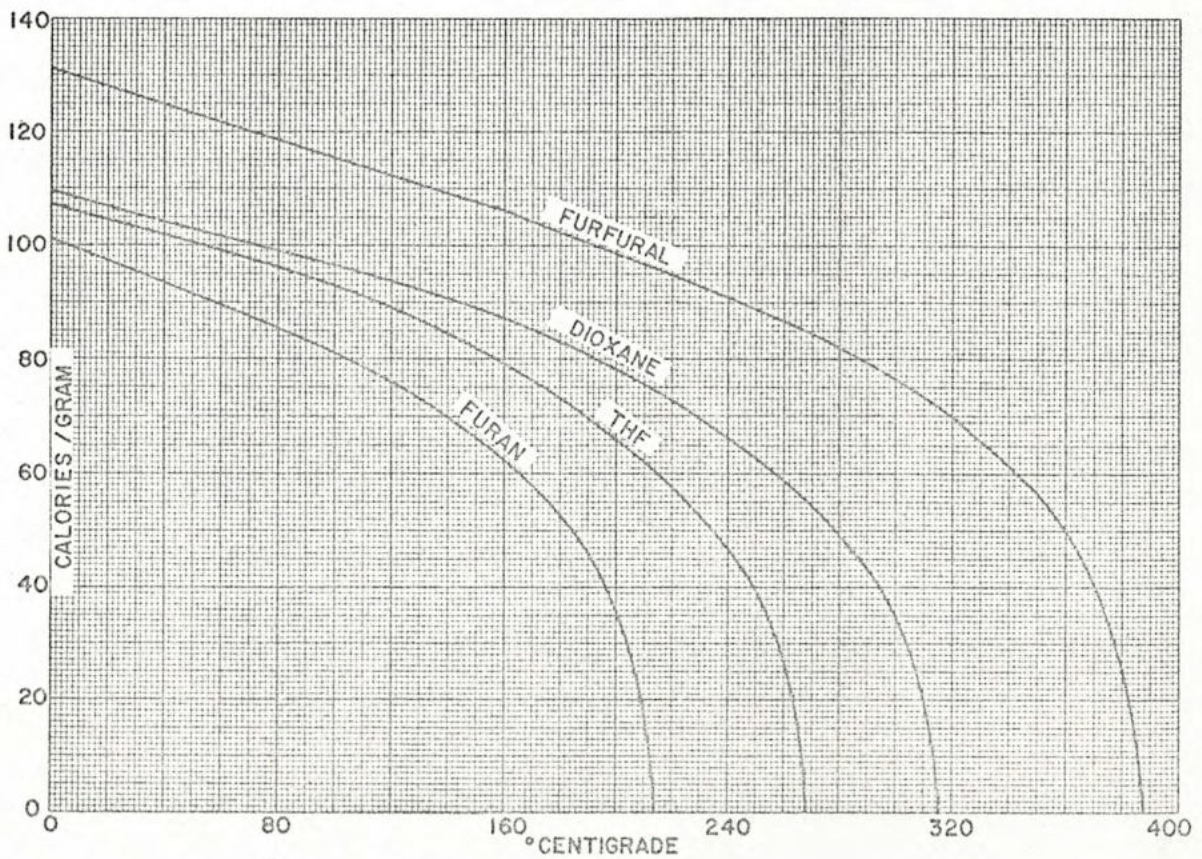


Fig. 32-3—Gives heat of vaporization for cyclic ethers from 0° C to +390° C.



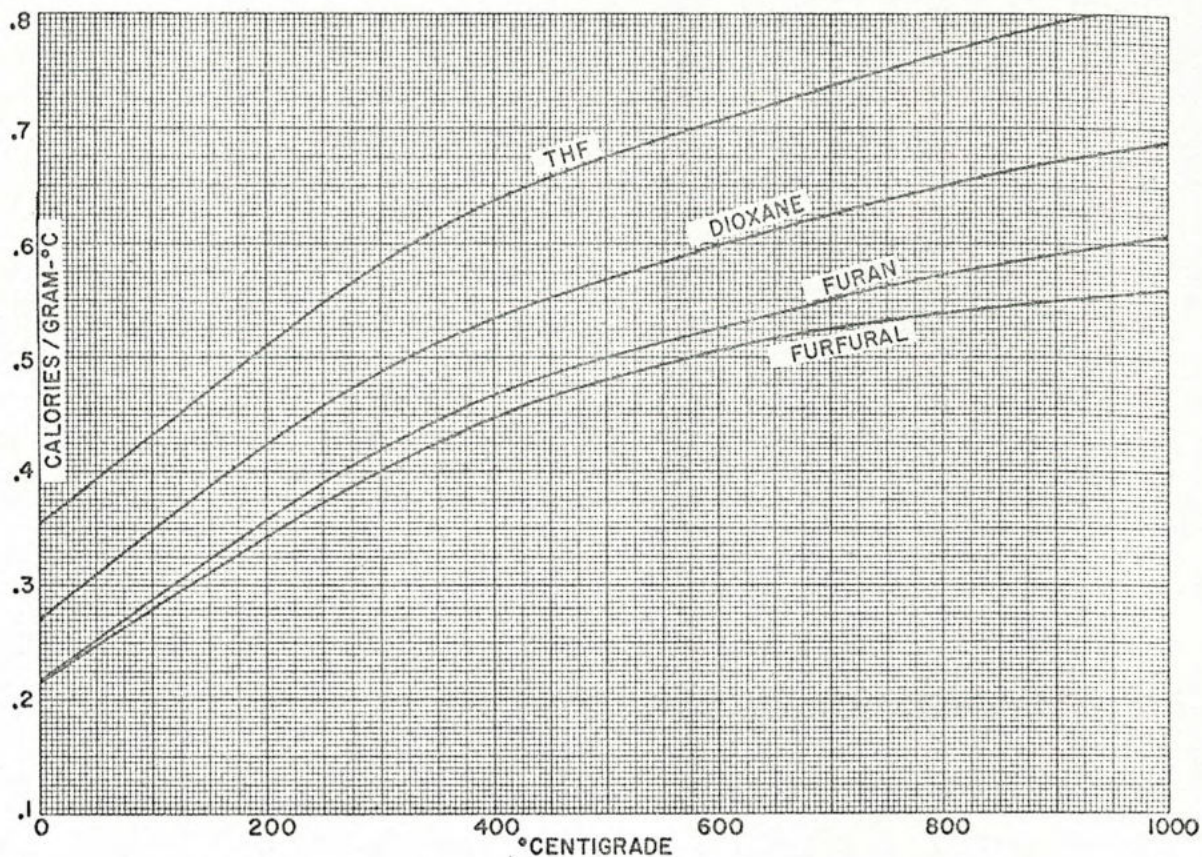


Fig. 32-4—Gives vapor heat capacity for cyclic ethers from 0° C to +1,000° C.

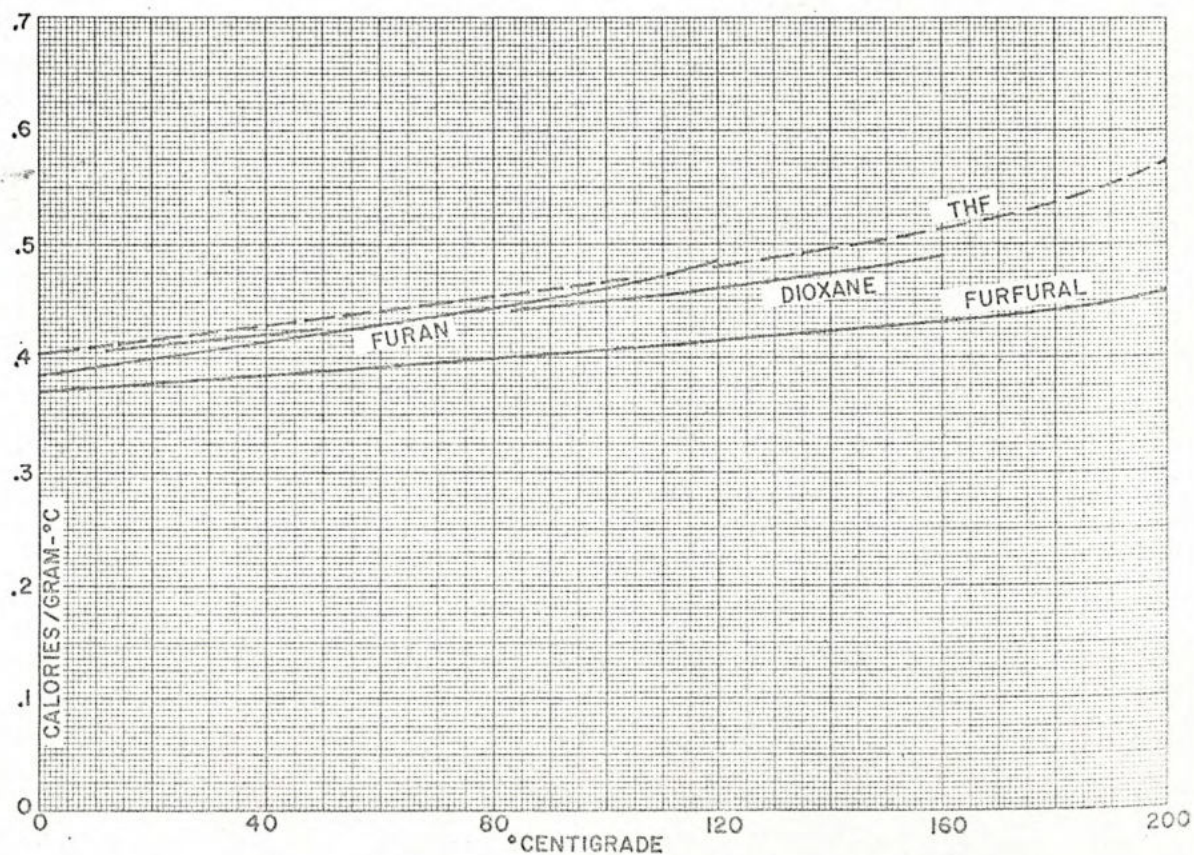


Fig. 32-5—Gives liquid heat capacity for cyclic ethers from 0° C to +200° C.



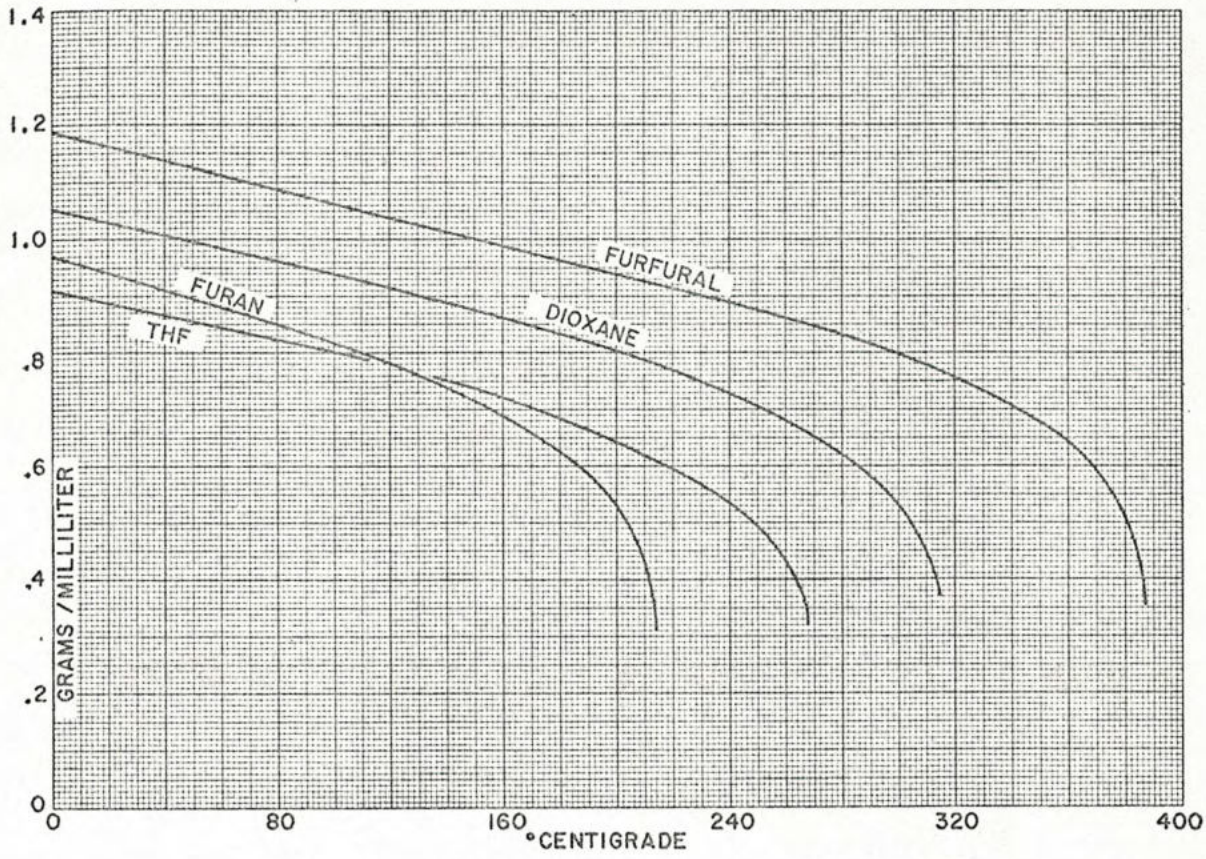


Fig. 32-6—Gives liquid density for cyclic ethers from 0° C to +380° C.

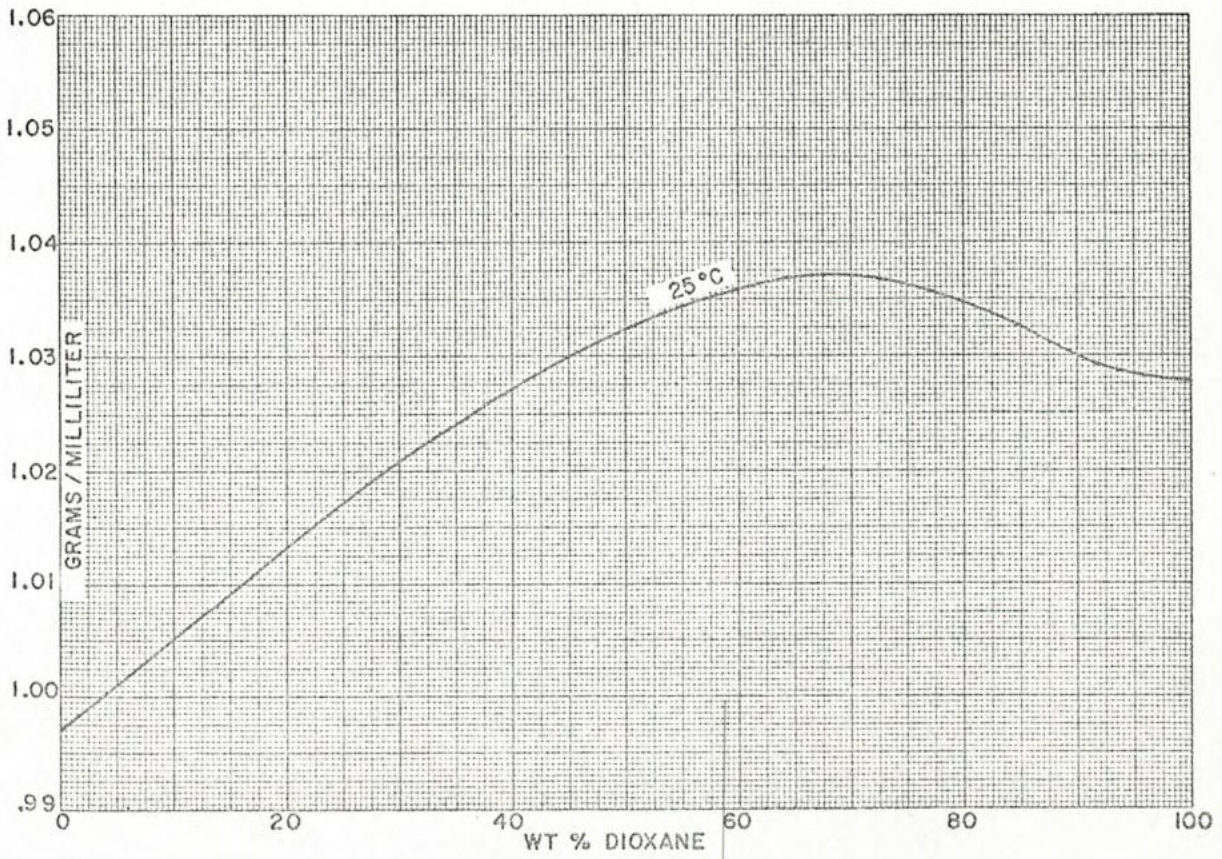


Fig. 32-7—Gives liquid density for dioxane-water solutions.



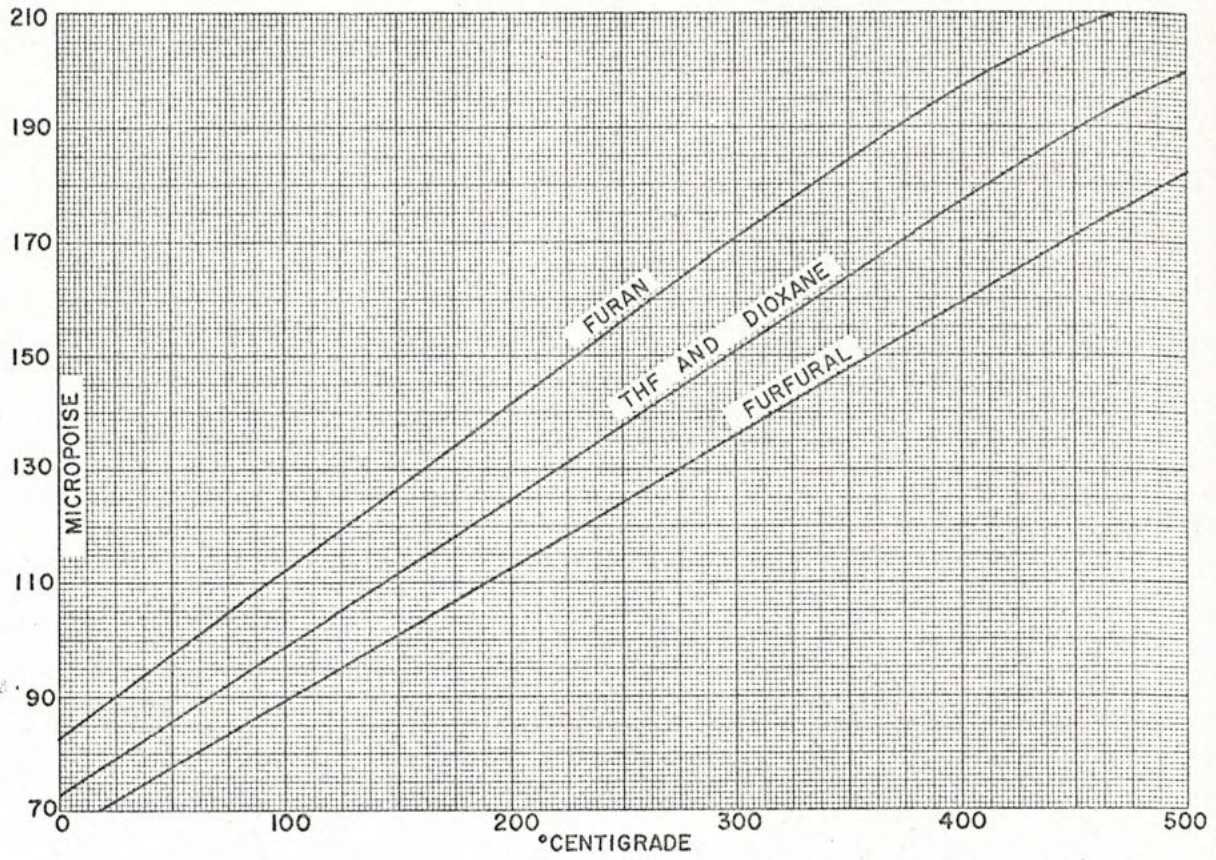


Fig. 32-8—Gives vapor viscosity for cyclic ethers from 0° C to +500° C.

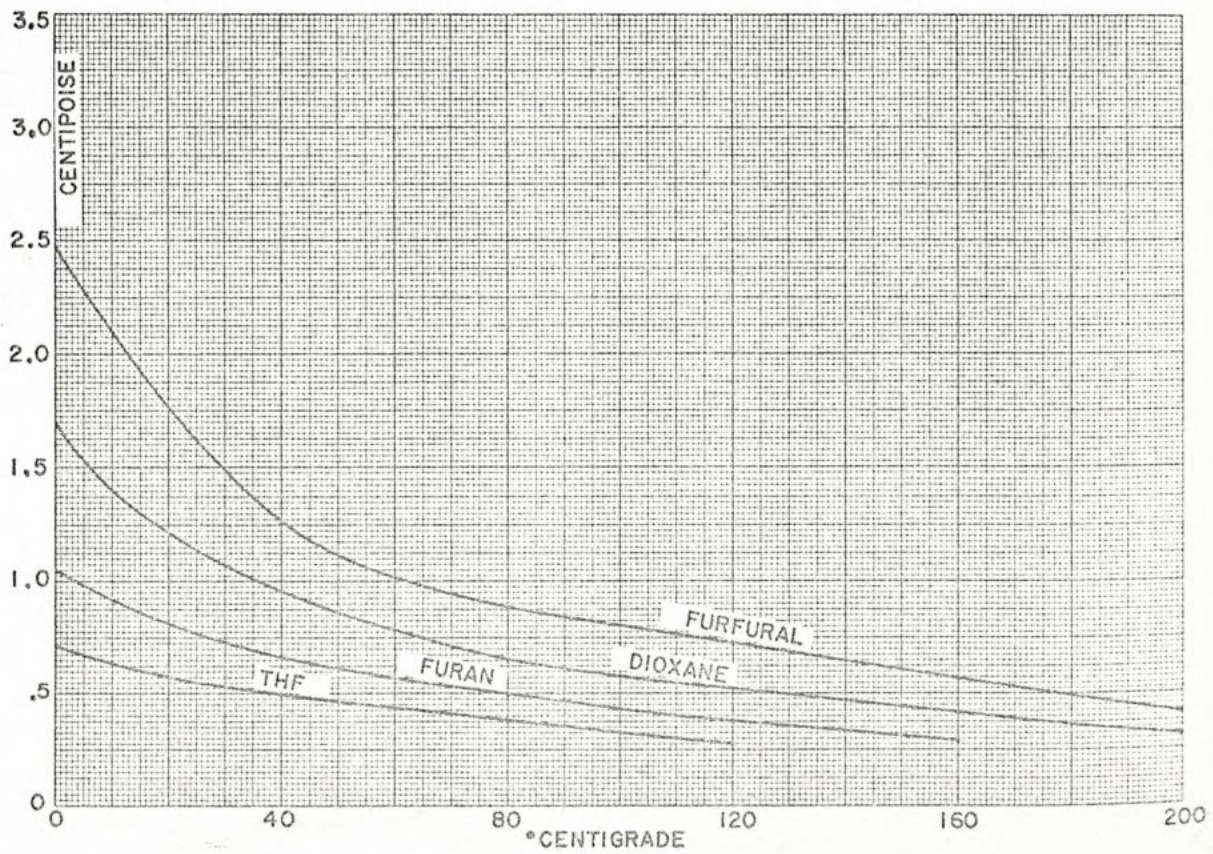


Fig. 32-9—Gives liquid viscosity for cyclic ethers from 0° C to +200° C.



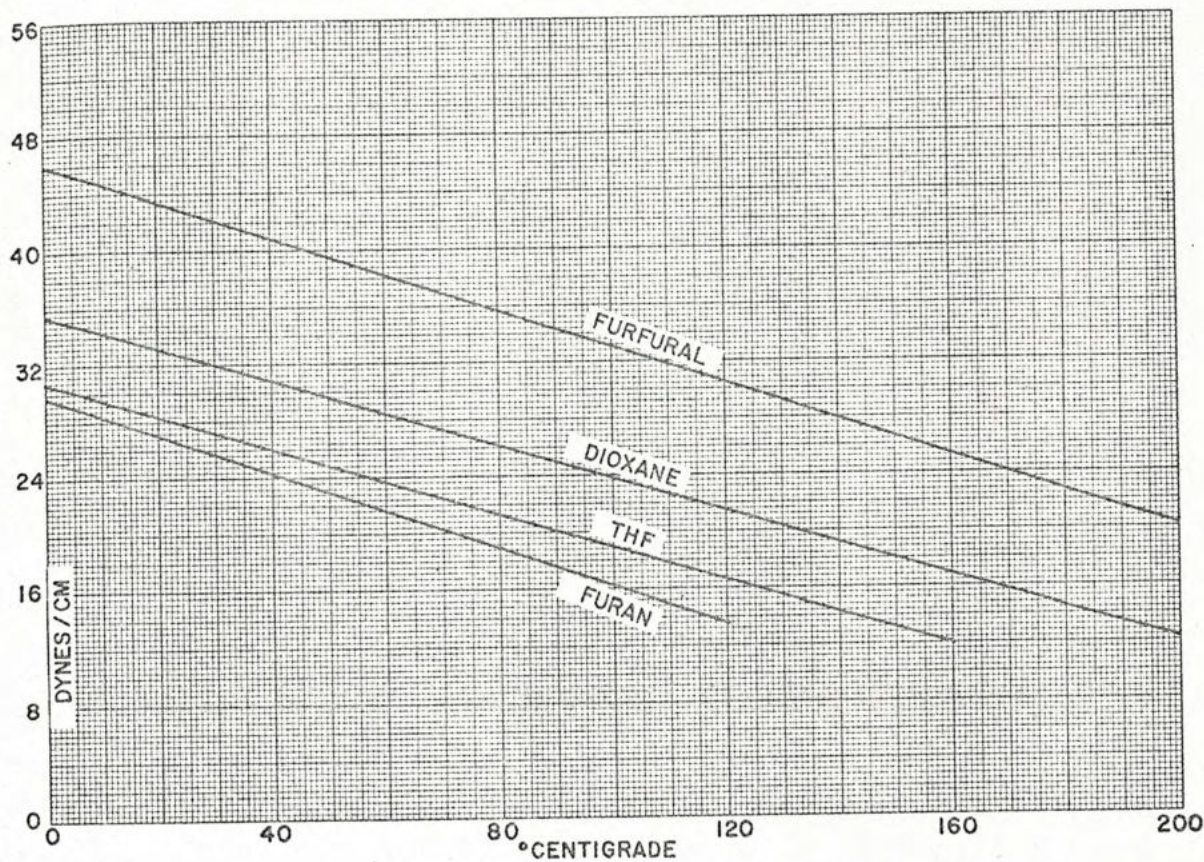


Fig. 32-10—Gives surface tension for cyclic ethers from 0° C to +200° C.

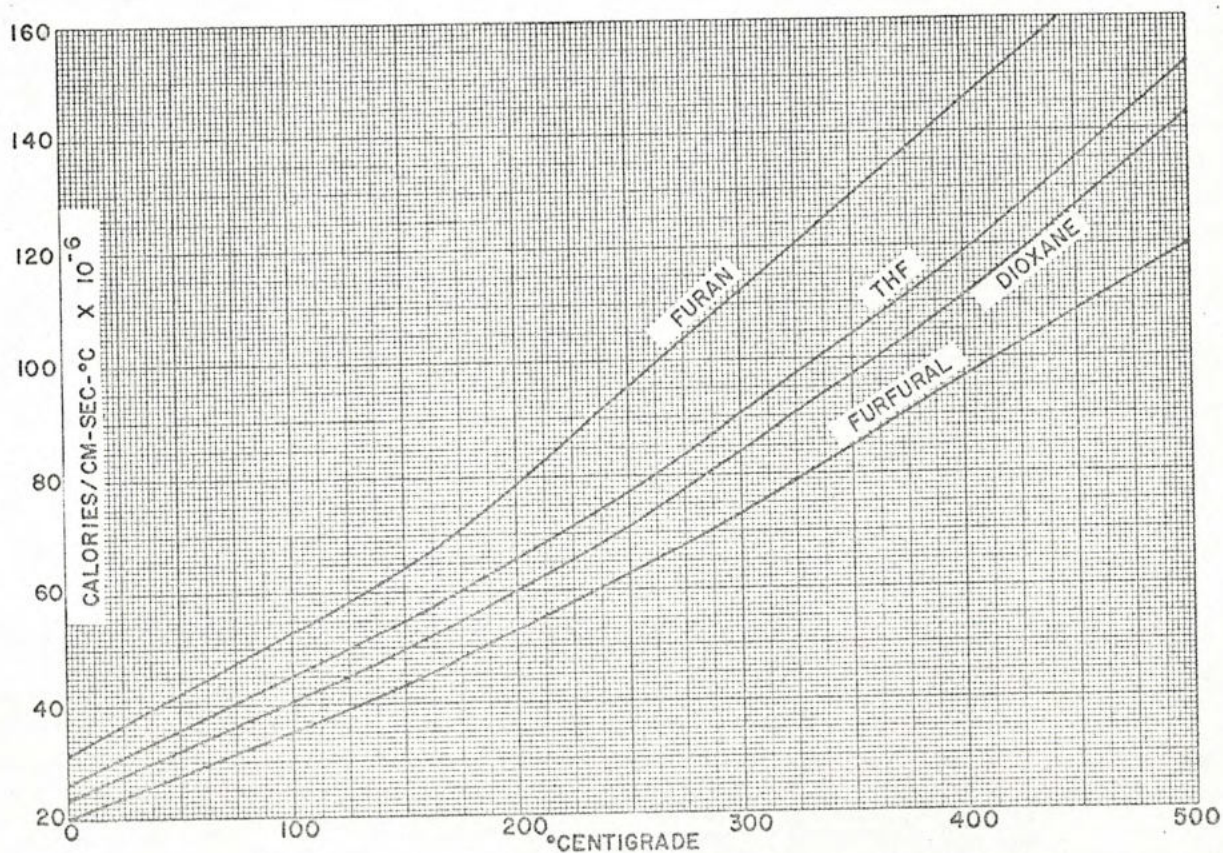


Fig. 32-11—Gives vapor thermal conductivity for cyclic ethers from 0° C to +500° C.



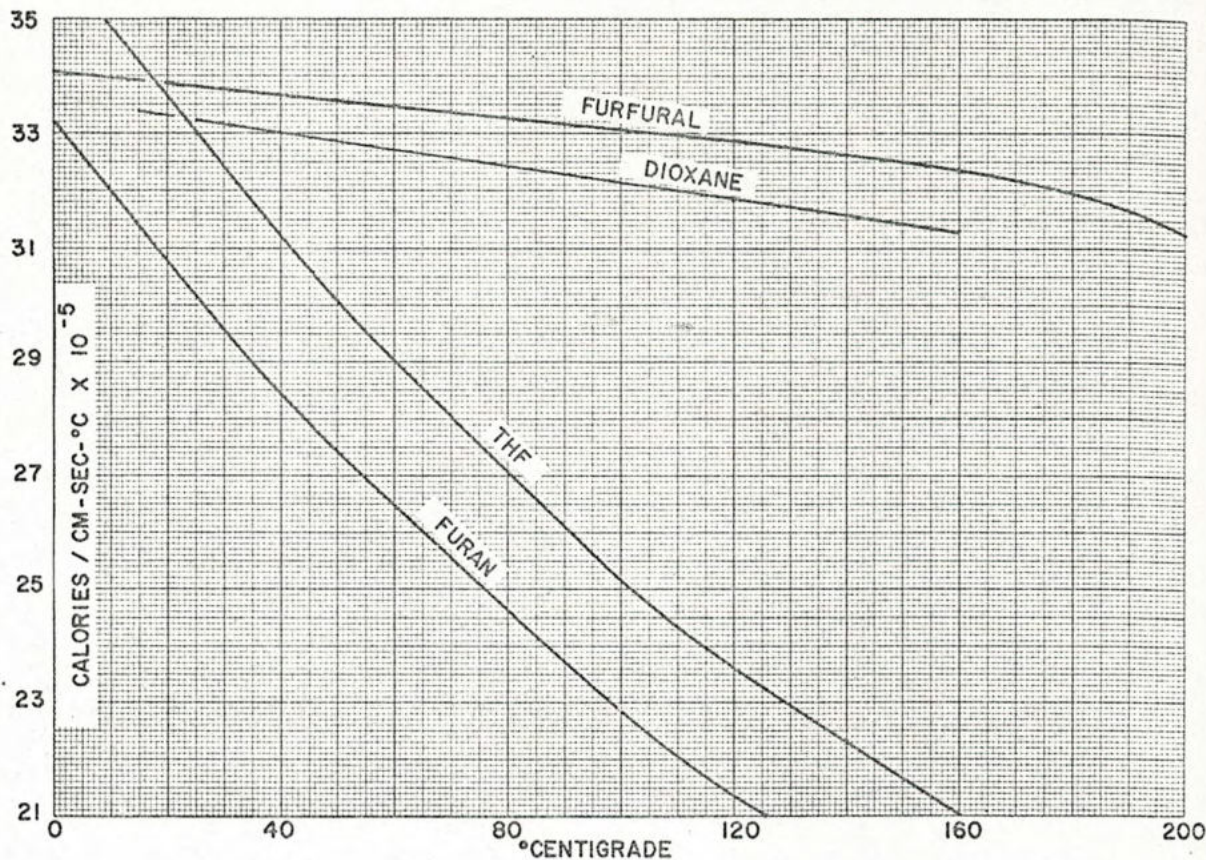


Fig. 32-12—Gives liquid thermal conductivity for cyclic ethers from 0° C to +200° C.

less. Graph 32-7 presents the data of Griff<sup>17</sup> and Schott<sup>18</sup> for the density of aqueous dioxane at 25° C.

**Viscosity.** The vapor viscosities were calculated by the technique developed by Bromley and Wilkes.<sup>19</sup>

Only the room temperature viscosities of dioxane and furfural have been measured.<sup>6</sup> Thomas's method was used to calculate the liquid viscosities.<sup>2</sup> The author modified the method since it gives low results for cyclic compounds. The probable error is 10-20 percent.

**Surface Tension.** The "International Critical Tables" report the surface tension of furfural from 20° to 160° C.<sup>13</sup> The literature presents data on dioxane from 0° to 90° C.<sup>6,12,20</sup> Sugden's equation was used to estimate the surface tensions of all four compounds. After modifying it for cyclic ethers, the average error for six experimental points was 0.5 percent.

**Thermal Conductivity.** Vines and Bennett<sup>21</sup> have measured the vapor thermal conductivities of dioxane from 100° to 150° C. These data were used to calculate the quasi-critical thermal conductivity constant for use in calculating the thermal conductivity at other temperatures by the equation of Owens and Thodos.<sup>22</sup> For the other three compounds, this constant had to be estimated, with a probable error of 10 percent.

The liquid thermal conductivities were calculated by the method proposed by Robbins and Kingrea.<sup>23</sup>

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Indexing Terms: Computations-4, Dioxane-9, Furfural-9, Furan-9, Liquid Phase-5, Physical Properties-7, Pressure-6, Properties Characterization-6, Temperature-6, Tetrahydrofuran-9, Vapor Phase-5.

Part 33 will appear in an early issue.