# Modification of Relative Volatilities by Addition of Solvent

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VAPOR-LIQUID equilibria were determined for the azeotropic binary system 2,4-dimethylpentane-benzene at 760, 400, and 250 mm. Hg pressure. Vapor-liquid equilibria were then determined at 400 mm. Hg pressure for the three ternary systems: the hydrocarbon binary system plus each of three polar solvents—hexylene glycol, aniline, and furfural. The main purpose of the study was to observe and correlate the effects of these extractive solvents on the hydrocarbon relative volatility. A Colburn vapor recirculating equilibrium still was used. All analyses were performed on a Beckman model GC-2 chromatograph. The error in the equilibrium determinations was less than 1%. The maximum temperature range experienced in this study, 36° C., was with hexylene glycol as the solvent.

## CHEMICALS USED

Three hydrocarbons were used in this study: 2,4 dimethylpentane (2,4 DMP), benzene, and methylcyclohexane (MCH). The MCH was used in the analysis procedure. All three hydrocarbons were obtained (Phillips Petroleum Co.) as pure grade chemicals (guaranteed 99.0 mole % minimum purity). All of these hydrocarbons were eluted on the chromatograph at 70° C.; they were all of approximately 99.5 mole % purity as determined by the chromatograms. These hydrocarbons were used without further purification.

The three solvents: hexylene glycol (Union Carbide Chemicals), aniline (J.T. Baker Chemical Co., reagent grade) and furfural (J.T. Baker Chemical Co., reagent grade) were all distilled under vacuum at about 15 to 1 reflux ratio. The vacuum-jacketed column was 3 feet by ¾ inch and was filled with glass helices. A small initial cut was discarded and purified chemicals were distilled at constant temperature. It was necessary to distill the furfural weekly to assure polymer-free samples for equilibrium determinations. The purified solvents were eluted at 130° C. on the chromatograph, and no contaminants were detected (this particular analytical apparatus could detect impurities of the order of 0.03%, or larger). Densities of the solvents as obtained by use of a 25-ml. pycnometer are shown in Table I.

Table I also summarizes some of the more important physical and chemical properties of the hydrocarbons and solvents.

## EXPERIMENTAL APPARATUS

A vapor recirculation still similar to one described by Jones, Schoenborn, and Colburn (*12*) was used. A Colburn still has many advantages such as rapid attainment of equilibrium, ease of operation and the small qauntity of material (about 25 ml.) required. Two pressure systems were attached to the still. One system was for the maintenance of 760 mm. Hg and the other for the two subatmospheric pressures. Pressure was maintained to within ±0.6 mm. Hg. A copper-constantan thermocouple, which was calibrated in place, gave temperature readings to ±0.15° C. or better.

## ANALYTICAL METHOD

All samples taken from the Colburn still were analyzed by means of a Beckman model GC-2 chromatograph and a Brown 1-mv. recorder. A 6-foot (by ¼ inch) Stainless steel, Carbowax 1000 column was used in the GC-2 along with a thermal conductivity cell. A Disc integrator (Disc Instruments, Inc.) was used to evaluate areas of the eluted peaks. The liquid samples were introduced into the chromatograph by a Beckman liquid sampler. At 70° C. the 2,4 DMP eluted in about 3 minutes and the benzene in about 15 minutes. It was of course necessary to obtain calibration curves for all of the systems to be analyzed. These calibrations were obtained by use of the area ratio technique. for a binary system, *A* and *B*, the area ratio for any sample is the area of *A* on the chromatogram divided by the area of *A* plus *B* on the chromatogram. A precision balance was used to prepare known samples for all the systems studied; these samples were eluted and the necessary area ratios were calculated. This calibration procedure is insensitive to changes in samples size and equipment conditions because all component areas are affected to approximately the same relative degree by any of these

Table I. Some Physical and Chemical Properties

| | | 2,4-DMP | Benzene | MCH | Hexylene Glycol | Aniline | Furfural |
|---|---|---|---|---|---|---|---|
| Normal B.P., ° C. | | 80.50 | 80.10 | 100.93 | 196 | 184.4 | 161.7 |
| B.P. at 400 mm. Hg | | 60.7 | 61.2 | ... | 177.1 | 161.1 | 141.8 |
| Molecular weight | | 100.2 | 78.1 | 98.2 | 118.2 | 93.1 | 96.1 |
| Density, g./ml. | 25° C. | ... | ... | ... | 0.920 | 1.019 | 1.157 |
| | 30° C. | ... | ... | ... | 0.916 | 1.014 | 1.151 |
| (*11*) | 20° C. | ... | ... | ... | ... | 1.022 | 1.160 |
| (*11*) | 17° C. | ... | ... | ... | 0.924 | ... | ... |
| Vapor pressure, mm. Hg[a] | 60° C. | 393 | 392 | ... | 1.0 | 6.0 | 13.4 |
| | 70° C. | 550 | 555 | ... | 2.2 | 10.4 | 22.4 |
| | 80° C. | 759 | 760 | ... | 4.3 | 18.3 | 36.3 |
| | 90° C. | 1010 | 1030 | ... | 7.9 | 29.0 | 56.9 |
| | 100° C. | 1320 | 1350 | ... | 14.0 | 45.5 | 87.0 |
| Tc, ° K.[b] | | 520 | 562 | ... | 744 | 699 | 656 |
| Pc, atm.[b] | | 520 | 48.6 | ... | 54.8 | 52.4 | 48.6 |
| Dipole Moment, debye[c] | | 0.0 | 0.2 | ... | 2.1 | 1.5 | 3.6 |
| Internal Press. at 400 mm. B.p., atm.[d] | | 1782 | 3040 | ... | 3590 | 4064 | 4400 |

[a] (*14, 20, 22*). [b] If not available, calculated by *17*. [c] (*24*). [d] Calculated (*4*).

changes. The calibration curves which were obtained in this fashion were accurate to at least root mean square deviations of 0.3% (binary systems) and 0.4% (the ternary system 2,4 DMP-MCH-benzene).

When analyzing any sample containing one of the three high-boiling extractive solvents, a back purging technique was used. Back purging means that after the low boiling components have eluted the helium flow is reversed, and the high boiling component is purged out the inlet port. To facilitate the calculations when back purging, it was necessary to add an internal standard to the original sample. MCH was used as the internal standard. By knowing both the weight per cent of MCH in the eluted solvent-free sample it was possible to calculate the composition of the original sample taken from the still. Back purging reduced the number of ternary calibration curves required to one set—the system: 2,4 DMP, MCH, and benzene. The internal standard must be chosen so that it elutes at a different time than any of the components in the original sample. The MCH eluted between 2,4 DMP and benzene.

This particular technique of back purging the high boiling solvent out the inlet port requires the use of an internal standard. In some circumstances, by use of appropriate valves and tubing, it is possible to back purge the high boiling component (or components) through the detector cell and thus obtain the eluted peak. When this is possible and desirable, an internal standard is not necessary.

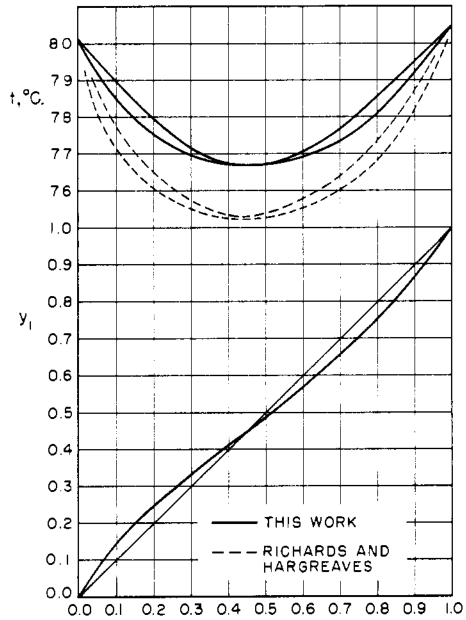

Figure 1. Comparison of *t-x-y* data with that obtained by Richards and Hargreaves
Component 1: 2,4-DMP Component 2: benzene

## HYDROCARBON BINARY SYSTEM

Richards and Hargreaves (*18*) studied the binary system 2,4 DMP-benzene in an Othmer liquid recirculation apparatus using an Anschutz thermometer. Their results at 757 mm. Hg pressure differ from this work as shown in Figure 1. Marschner and Cropper (*13*) studied the boiling points of benzene azeotropes in laboratory fractionating columns. Marschner and Cropper checked the 2,4 DMP-benzene azeotrope several times and always obtained 76.7° C. at 760 mm. Hg pressure. This is in agreement with the temperature obtained in this study. Richards and Hargreaves perhaps had the Anschutz thermometer improperly placed in the boiling surface and hence read consistent but erroneous temperatures. This points out one of the advantages of calibrating a temperature measuring device in place with pure compounds. If this is done properly there is never any question as to the positioning of the device for correct readings of unknown temperatures.

One purpose in obtaining experimental data at three pressures was to observe the effect of pressure on the azeotropic composition. For 250, 400, and 760 mm. Hg pressure there was no significant change in the azeotropic composition (Figure 2). Redlich and Kister consistency tests (*16*) of the binary system were in error by 2.4% (250 mm. Hg), 2.8% (400 mm. Hg), and 4.7% (760 mm. Hg). The temperature-composition curves at 760 mm. Hg pressure (Figure 3), activity coefficient-composition curves, (Figure 4), and the relative volatility-composition relationship at 760 mm. Hg (Figure 5) are given. The results at 250 and 400 mm. Hg pressure are similar to those at 760 mm. Hg pressure. Both the van Laar and Margules binary equations (*25*) represented the data. The experimental data for the hydrocarbon binary system are shown in Table II. Table III summarizes the information on the binary hydrocarbon system at all three pressures.

## BINARY SYSTEMS

A binary system containing the solvents whose components exhibits large differences in volatility has several unique features. If volatility difference is large enough (as in this study) it is difficult, if not impossible, to obtain meaningful experimental van Laar (or Margules) constants. At low values of $x_1$ (high volatility component) the activity coefficient of component 2 is near unity, thus seriously limiting the accuracy of the calculations. At higher values of $x_1$ where $\gamma_2$ is significantly different from unity, $y_1$ approaches unity. With either $\gamma_2$ or $y_1$ equal or close to unity it is not possible to calculate accurately the binary constants.

Figure 2. The *x-y* data of the hydrocarbon binary system at three pressures
Component 1: 2,4-DMP Component 2: benzene

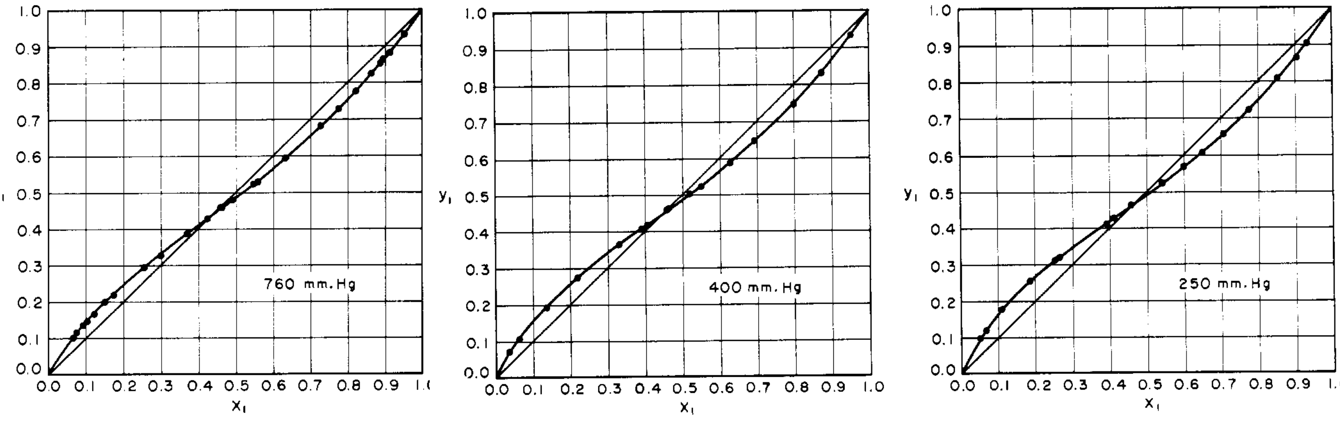

Table II. Experimental Data for the Hydrocarbon Binary System at Three Pressures

| $t$, ° C. | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $\alpha_{12}$ |
|---|---|---|---|---|---|
| | | 760 Mm. Hg Pressure | | | |
| 80.5 | 1.000 | 1.000 | | | |
| 79.8 | 0.951 | 0.933 | 1.00 | 1.38 | 0.72 |
| 79.3 | 0.912 | 0.881 | 1.00 | 1.38 | 0.71 |
| 79.1 | 0.893 | 0.861 | 1.00 | 1.34 | 0.74 |
| 79.1 | 0.884 | 0.850 | 1.00 | 1.33 | 0.74 |
| 78.8 | 0.861 | 0.823 | 1.01 | 1.33 | 0.75 |
| 78.3 | 0.821 | 0.773 | 1.01 | 1.34 | 0.74 |
| 77.9 | 0.774 | 0.726 | 1.02 | 1.30 | 0.77 |
| 77.5 | 0.727 | 0.681 | 1.02 | 1.27 | 0.80 |
| 77.0 | 0.633 | 0.594 | 1.04 | 1.22 | 0.85 |
| 77.0 | 0.632 | 0.591 | 1.04 | 1.22 | 0.84 |
| 76.7 | 0.558 | 0.529 | 1.06 | 1.18 | 0.89 |
| 76.8 | 0.545 | 0.521 | 1.07 | 1.17 | 0.91 |
| 76.7 | 0.489 | 0.475 | 1.09 | 1.14 | 0.94 |
| 76.6 | 0.460 | 0.453 | 1.11 | 1.13 | 0.97 |
| 76.7 | 0.457 | 0.453 | 1.11 | 1.12 | 0.98 |
| 76.7 | 0.422 | 0.425 | 1.13 | 1.11 | 1.01 |
| 76.8 | 0.369 | 0.385 | 1.17 | 1.08 | 1.07 |
| 76.9 | 0.299 | 0.327 | 1.22 | 1.06 | 1.14 |
| 77.1 | 0.253 | 0.291 | 1.27 | 1.04 | 1.21 |
| 77.9 | 0.171 | 0.216 | 1.37 | 1.01 | 1.34 |
| 77.9 | 0.148 | 0.199 | 1.45 | 1.01 | 1.43 |
| 78.3 | 0.121 | 0.165 | 1.46 | 1.00 | 1.43 |
| 78.4 | 0.103 | 0.146 | 1.51 | 1.00 | 1.49 |
| 78.4 | 0.101 | 0.146 | 1.54 | 1.00 | 1.52 |
| 78.5 | 0.090 | 0.131 | 1.54 | 1.00 | 1.52 |
| 78.8 | 0.073 | 0.111 | 1.60 | 1.00 | 1.58 |
| 78.9 | 0.065 | 0.099 | 1.60 | 1.00 | 1.58 |
| 80.1 | 0 | 0 | | | |
| | | 400 Mm. Hg Pressure | | | |
| 60.6 | 1.000 | 1.000 | | | |
| 60.0 | 0.953 | 0.931 | 0.99 | 1.50 | 0.66 |
| 59.2 | 0.870 | 0.830 | 1.00 | 1.38 | 0.73 |
| 58.5 | 0.799 | 0.743 | 1.00 | 1.38 | 0.73 |
| 57.8 | 0.691 | 0.645 | 1.03 | 1.27 | 0.81 |
| 57.5 | 0.627 | 0.588 | 1.04 | 1.24 | 0.85 |
| 57.5 | 0.548 | 0.521 | 1.06 | 1.19 | 0.90 |
| 57.4 | 0.519 | 0.502 | 1.08 | 1.16 | 0.93 |
| 57.4 | 0.461 | 0.461 | 1.12 | 1.12 | 1.00 |
| 57.1 | 0.459 | 0.459 | 1.13 | 1.13 | 1.00 |
| 57.4 | 0.407 | 0.415 | 1.14 | 1.11 | 1.03 |
| 57.7 | 0.389 | 0.404 | 1.15 | 1.08 | 1.06 |
| 57.5 | 0.331 | 0.361 | 1.21 | 1.07 | 1.14 |
| 58.1 | 0.219 | 0.271 | 1.35 | 1.02 | 1.33 |
| 58.8 | 0.134 | 0.192 | 1.52 | 0.99 | 1.54 |
| 59.4 | 0.063 | 0.108 | 1.79 | 0.99 | 1.80 |
| 60.0 | 0.037 | 0.070 | 1.93 | 0.99 | 1.96 |
| 60.6 | 0 | 0 | | | |
| | | 250 Mm. Hg Pressure | | | |
| 47.5 | 1.000 | 1.000 | | | |
| 46.6 | 0.931 | 0.901 | 1.00 | 1.51 | 0.67 |
| 46.1 | 0.903 | 0.861 | 1.01 | 1.53 | 0.66 |
| 45.9 | 0.865 | 0.817 | 1.01 | 1.46 | 0.70 |
| 45.1 | 0.776 | 0.721 | 1.02 | 1.39 | 0.75 |
| 44.6 | 0.707 | 0.657 | 1.04 | 1.33 | 0.79 |
| 44.5 | 0.650 | 0.606 | 1.05 | 1.28 | 0.83 |
| 44.2 | 0.603 | 0.567 | 1.07 | 1.26 | 0.86 |
| 44.3 | 0.544 | 0.521 | 1.08 | 1.21 | 0.91 |
| 44.3 | 0.459 | 0.460 | 1.14 | 1.15 | 1.00 |
| 44.2 | 0.413 | 0.423 | 1.16 | 1.13 | 1.04 |
| 44.5 | 0.391 | 0.411 | 1.18 | 1.10 | 1.09 |
| 44.7 | 0.268 | 0.319 | 1.33 | 1.05 | 1.28 |
| 44.8 | 0.257 | 0.311 | 1.35 | 1.05 | 1.30 |
| 45.0 | 0.188 | 0.251 | 1.47 | 1.03 | 1.45 |
| 45.3 | 0.113 | 0.177 | 1.71 | 1.03 | 1.69 |
| 45.8 | 0.070 | 0.119 | 1.82 | 1.03 | 1.79 |
| 46.8 | 0.052 | 0.094 | 1.86 | 1.00 | 1.89 |
| 47.7 | 0 | 0 | | | |

Table III. Summary of Information for the Hydrocarbon Binary System

| | | 760 Mm. | 400 Mm. | 250 Mm. |
|---|---|---|---|---|
| Azeotrope, ° C. | | 76.7 | 57.3 | 44.2 |
| Azeotrope, $x_1$(2,4-DMP) | | 0.440 | 0.460 | 0.460 |
| Redlich-Kister test, error % | | 4.7 | 2.8 | 2.4 |
| van Laar A | | 0.240 | 0.284 | 0.291 |
| B | | 0.158 | 0.170 | 0.199 |
| RMS[a], % | $x_1 = 0.05$ to 0.95 | 1.0 | 1.0 | 1.5 |
| | $x_1 = 0.10$ to 0.90 | 0.9 | 0.8 | 0.9 |
| Margules A | | 0.288 | 0.238 | 0.270 |
| B | | 0.151 | 0.154 | 0.191 |
| RMS[a], % | $x_1 = 0.05$ to 0.95 | 1.1 | 1.4 | 2.2 |
| | $x_1 = 0.10$ to 0.90 | 0.8 | 1.1 | 1.3 |
| Activity Coefficients | | | | |
| 2,4-DMP $_1$ | $x_1 = 0.1$ | 1.52 | 1.64 | 1.72 |
| | $x_1 = 0.5$ | 1.09 | 1.09 | 1.11 |
| | $x_1 = 0.9$ | 1.00 | 1.00 | 1.00 |
| Benzene $_2$ | $x_1 = 0.1$ | 1.00 | 1.00 | 1.01 |
| | $x_1 = 0.5$ | 1.15 | 1.15 | 1.17 |
| | $x_1 = 0.9$ | 1.36 | 1.45 | 1.50 |
| RV[b], $\alpha_{12}$ | $x_1 = 0.25$ | 1.21 | 1.27 | 1.31 |
| | $x_1 = 0.50$ | 0.94 | 0.96 | 0.96 |
| | $x_1 = 0.75$ | 0.78 | 0.77 | 0.76 |

[a] Root mean square deviation in per cent. [b] Relative volatility.

Table IV. Experimental Data on the Miscible Hydrocarbon-Solvent Binary Systems at 400 Mm. Hg Pressure

| | $t$, ° C. | $x_3$ | $y_3$ |
|---|---|---|---|
| 2,4-DMP $_1$-Hexylene Glycol $_3$ | 147.7 | 0.980 | 0.325 |
| | 127.0 | 0.952 | 0.163 |
| | 69.5 | 0.790 | 0.010 |
| | 66.6 | 0.724 | 0.004 |
| Benzene $_2$-Hexylene Glycol $_3$ | 137.1 | 0.958 | 0.215 |
| | 121.1 | 0.940 | 0.119 |
| | 77.1 | 0.673 | 0.010 |
| Benzene $_2$-Aniline $_3$ | 140.9 | 0.961 | 0.481 |
| | 135.7 | 0.956 | 0.411 |
| | 120.2 | 0.920 | 0.203 |
| Benzene $_2$-Furfural $_3$ | 112.7 | 0.922 | 0.386 |
| | 109.3 | 0.899 | 0.285 |
| | 100.3 | 0.861 | 0.200 |

Note: Inferior numbers in parentheses indicate the subscript used in the tabular headings—e.g., $y_3$ is the vapor composition with respect to furfural under the last section in the table.

However, it is possible to obtain van Laar constants by a relatively recent correlation technique developed by Finch (*4*). This correlation was developed to handle polar-nonpolar systems, and it proved extremely valuable in this work. Two binary systems were immiscible: 2,4 DMP-aniline and 2,4 DMP-furfural. No experimental data were obtained on these two systems. The Finch correlation gave van Laar constants which reproduced the experimental data on the miscible binary systems (Table IV) and adequately represented the immiscible binary systems (as indicated by the shape of the $x$-$y$ curves). These van Laar constants are shown in Table V.

## TERNARY SYSTEMS

All ternary experimental data were obtained in such a way that the hydrocarbon relative volatility ($\alpha'$) could be shown as a function of the mole fraction of the solvent in the liquid phase ($x_3$). Because of liquid phase miscibility limitations the mole fractions of aniline and furfural were not allowed to exceed about 0.7 and 0.6, respectively. The experimental data for the three ternary systems at 400 mm. Hg pressure are shown in Table VI.

Many studies of the effect of extractive solvents on binary systems have appeared (*1, 2, 3, 5, 6, 8, 9, 21, 23*), but in many cases the entire range of solvent concentration was not studied. In industrial practice where extractive distillation is used, the concentration of the solvent is always considerably less than 100%. Although valuable information can be gained from a study of several solvents at one

## Hydrocarbon Binary System at 760 mm. Hg Pressure

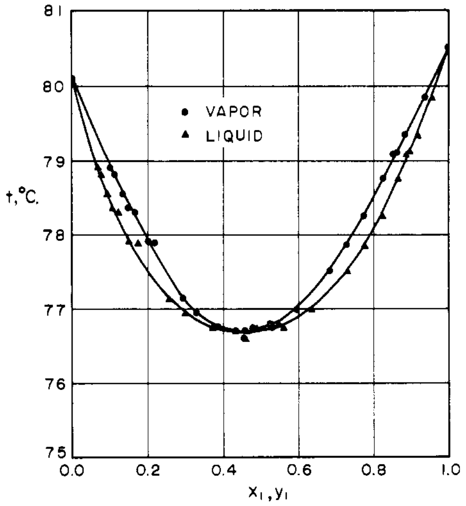

Figure 3. The *t*-*x*-*y* data
Component 1: 2,4-DMP
Component 2: benzene

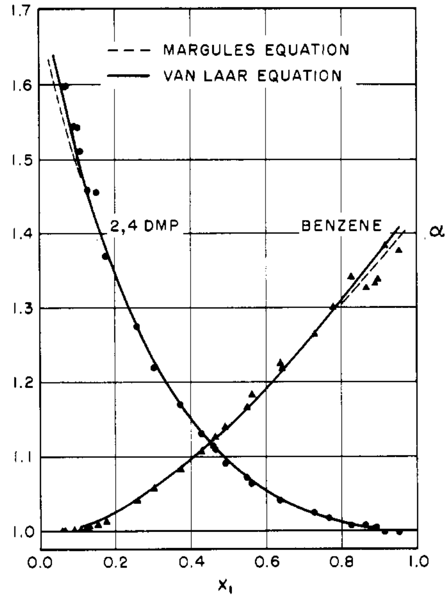

Figure 4. The $\gamma$ – $x$ data

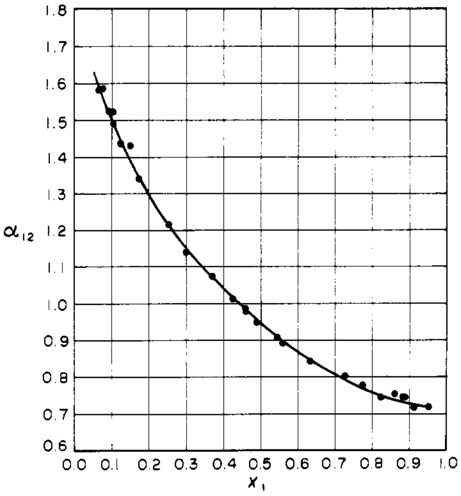

Figure 5. The $\alpha$ – $x$ data

solvent concentration (usually 90 to 99%), it is also necessary that detailed studied of particular extractive systems be undertaken.

When considering isobaric vapor-liquid equilibria, there appear to be three relatively distinct types of extractive systems. The system normally encountered may be represented by the ternary system: 2,4-DMP–benzene–hexylene glycol (Figure 6). Here the component relative volatility shows a sustained, gradual increase as solvent concentration in the liquid increases. The second system displays a maximum relative volatility-solvent concentration curve; that is, at some intermediate concentration of solvent the relative volatility, $\alpha'$, reaches a maximum and then decreases in value at higher solvent concentrations (*9*, *15*). A third system appears to be represented by the ternary systems: 2,4-DMP–benzene–aniline and 2,4-DMP–benzene–furfural (Figures 7 and 8). This third type of system is characterized by a very rapid and continual rise in component relative volatility. The apparent reason for this phenomenon is the immiscibility which exists between 2,4-DMP and the solvent (aniline or furfural). As this immiscible region is approached the component relative volatility increases quite rapidly.

All three of the solvents studied eliminated the binary system azeotrope. With hexylene glycol about 33 mole % solvent was required (Figure 9); with aniline about 20 mole % (Figure 10); and with furfural about 20 mole % (Figure 11). The $\alpha'$ curves with aniline and furfural solvents are concave upward. The $\alpha'$ curves at higher concentrations of 2,4-DMP ($x_1' = 0.50$ and 0.75) are concave upward with the hexylene glycol solvent. This change of curvature from concave downward ($x_1' = 0.25$) to concave upward indicates a trend toward immiscibility between 2,4-DMP and hexylene glycol. As has been pointed out (*19*), the effectiveness of an extractive solvent can sometimes be directly related to the degree of approach to immiscibility. Both solvent polarity and internal pressure have been discussed as important characteristics in evaluating potential extractive solvents (*7*, *10*). The values of solvent internal pressure and dipole moment (Table I) do suggest that aniline and furfural would be better extractive agents than hexylene glycol.

## Binary System Relative Volatility

$P_t$ = 400 Mm. Hg

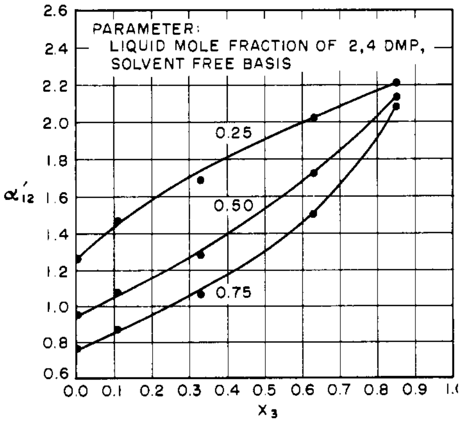

Figure 6. Hexalene glycol is the solvent

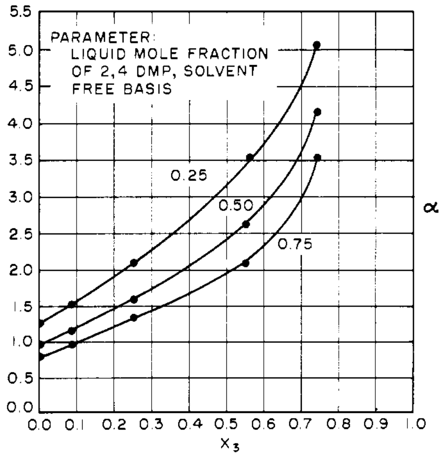

Figure 7. Aniline is the solvent

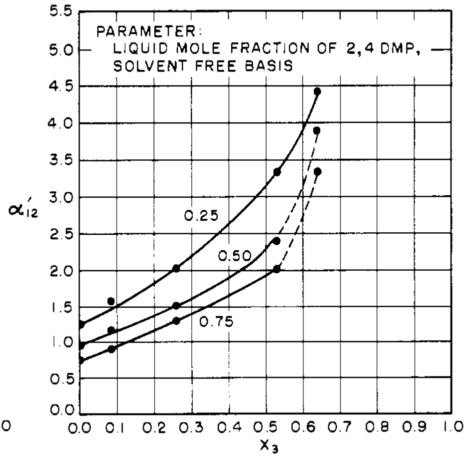

Figure 8. Furfural is the solvent

## Effect of Solvent in the Binary System Vapor-liquid Equilibria (Solvent-free Basis)

$P_t$ = 400 Mm. Hg

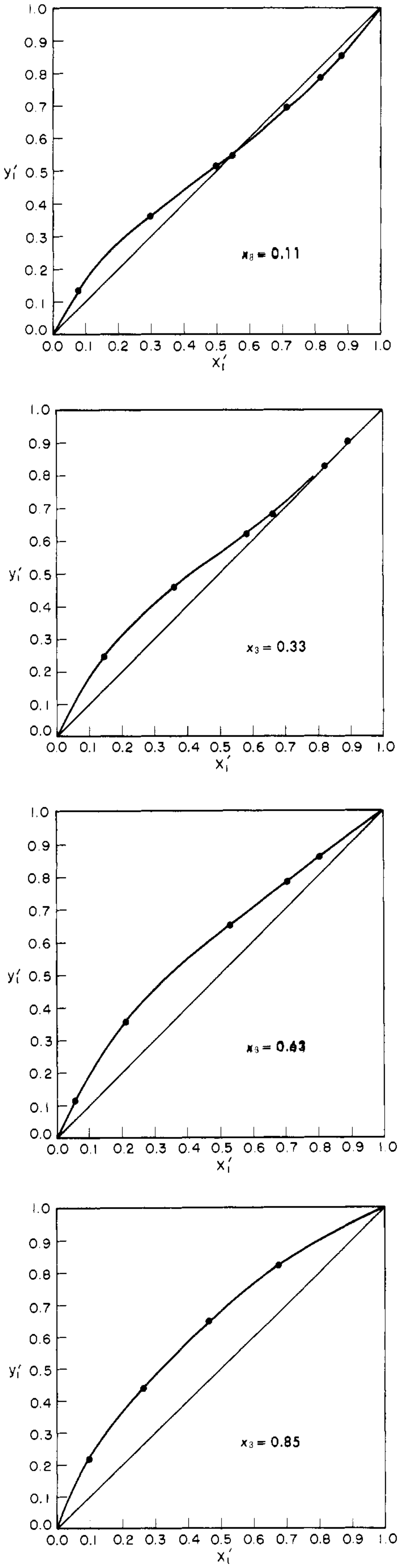

Figure 9. Hexylene glycol is the solvent

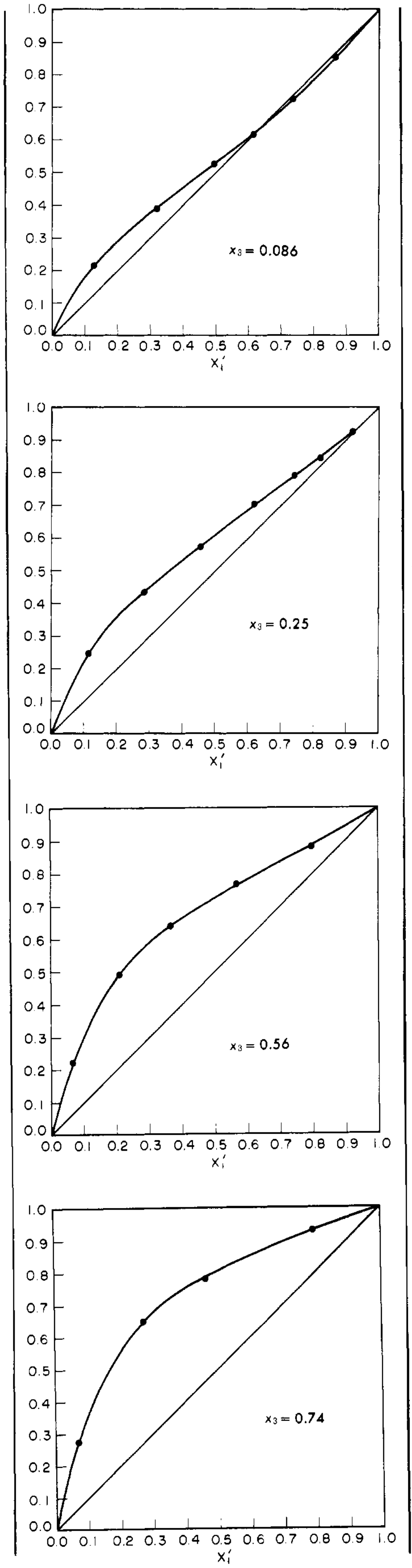

Figure 10. Aniline is the solvent

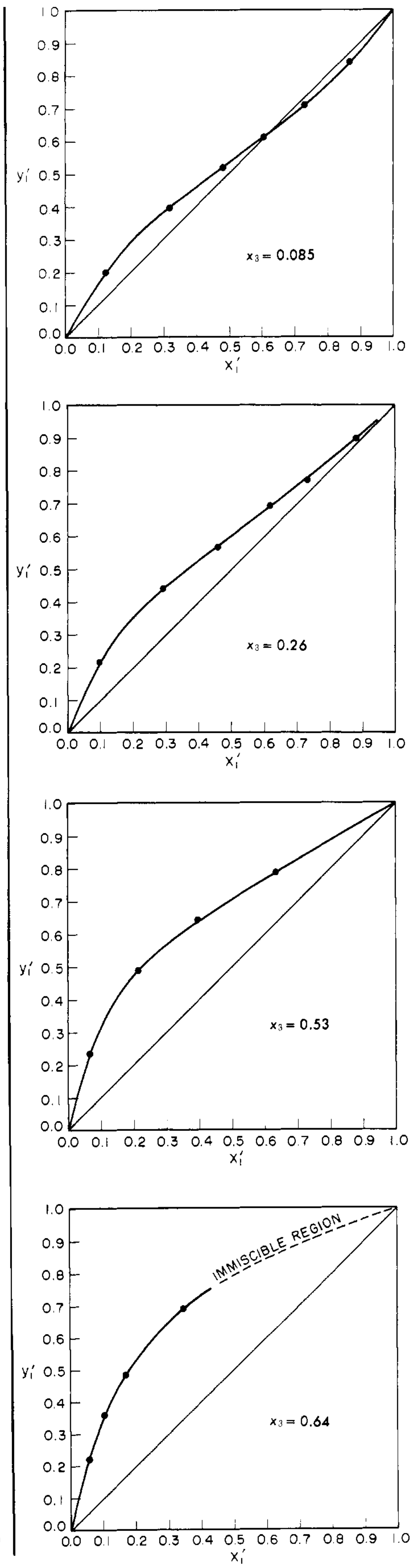

Figure 11. Furfural is the solvent

Table V. Calculated Binary System van Laar Constants using the Finch Correlation

| | $A$ | $B$ | Miscible |
|---|---|---|---|
| 2,4-DMP–hexylene glycol | 0.55 | 1.18 | yes |
| 2,4-DMP–aniline | 0.88 | 1.37 | no |
| 2,4-DMP–furfural | 0.55 | 1.36 | no |
| Benzene-hexylene glycol | 0.31 | 0.59 | yes |
| Benzene-aniline | 0.40 | 0.61 | yes |
| Benzene-furfural | 0.20 | 0.79 | yes |

## TERNARY CORRELATION

The very nature of many extractive systems is such that some of the binary systems may be immiscible. In seeking to correlate the resultant ternary systems under such conditions it was expedient to utilize the Finch correlation. As was mentioned earlier, experimental binary constants may not be available from miscible systems either (e.g., benzene–hexylene glycol) because of the large volatility difference. By use of these binary van Laar constants, the ternary van Laar equation (*25*),

$$\log \gamma_1 = \frac{x_2^2 A_{12}\left(\frac{A_{21}}{A_{12}}\right)^2 + x_3^2 A_{13}\left(\frac{A_{31}}{A_{13}}\right)^2 + x_2 x_3 \frac{A_{21}}{A_{12}}\frac{A_{31}}{A_{13}}\left(A_{12} + A_{13} - A_{32}\frac{A_{13}}{A_{31}}\right)}{\left(x_1 + x_2\frac{A_{21}}{A_{12}} + x_3\frac{A_{31}}{A_{13}}\right)^2} \qquad (1)$$

and an empirical correction factor it was possible to correlate the ternary experimental data. By use of Equation 2, root mean square deviations on experimental relative volatilities were 8.6% (hexylene glycol system), 4.7% (aniline system), and 6.1% (furfural system).

$$\left(\frac{\alpha'}{\alpha'_v}\right)^{1/3} = (a + bx'_1)\, x_3 + 1.00 \qquad (2)$$

$\alpha'$ = experimental component relative volatility
$\alpha'_v$ = component relative volatility as obtained by use of the ternary van Laar equation
$a$ and $b$ = empirical constants (Figures 12 and 13)
$x'_1$ = liquid mole fraction of 2,4-DMP (most volatile component) on a solvent-free basis
$x_3$ = liquid mole fraction of the solvent

The two empirical constants $a$ and $b$ are functions of the system (Table &) and they are shown to correlate with certain physical properties (Figures 12 and 13). The deviation of 8.6% on the hexylene glycol system was due to the change in curvature on the $x'_1 = 0.25$ curve.

In binary van Laar constants used in Equation 1, random variations of 10% caused no change in the relative volatility, $\alpha'_v$. This insensitivity to the constants is probably due to the large volatility differences in two of the three binary systems in each ternary system. Thus, the Finch correlation can be used with considerable confidence because of the insensitivity of the final correlation to the binary van Laar constants.

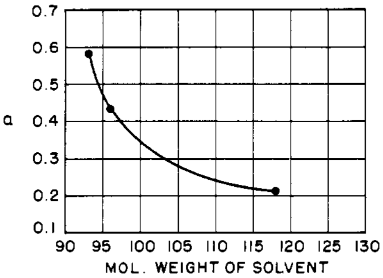

Figure 12. Empirical constant "a" is a function of solvent molecular weight

Table VI. Experimental Data for the Ternary Systems at 400 Mm. Hg Pressure

| $t$, ° C. | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $x'_1$ | $y'_1$ |
|---|---|---|---|---|---|---|
| System: 2,4-DMP$_1$–Benzene$_2$–Hexylene Glycol$_3$ | | | | | | |
| 60.6 | 0.069 | 0.824 | 0.130 | 0.868 | 0.077 | 0.130 |
| 60.5 | 0.070 | 0.832 | 0.134 | 0.864 | 0.078 | 0.134 |
| 58.5 | 0.264 | 0.625 | 0.359 | 0.638 | 0.297 | 0.360 |
| 58.4 | 0.265 | 0.623 | 0.362 | 0.637 | 0.298 | 0.362 |
| 58.2 | 0.442 | 0.447 | 0.509 | 0.482 | 0.497 | 0.514 |
| 58.1 | 0.493 | 0.410 | 0.533 | 0.446 | 0.546 | 0.544 |
| 59.0 | 0.641 | 0.255 | 0.693 | 0.307 | 0.715 | 0.693 |
| 59.4 | 0.719 | 0.162 | 0.785 | 0.215 | 0.816 | 0.785 |
| 60.1 | 0.777 | 0.106 | 0.852 | 0.148 | 0.880 | 0.852 |
| 61.7 | 0.096 | 0.553 | 0.242 | 0.752 | 0.148 | 0.243 |
| 60.0 | 0.229 | 0.411 | 0.449 | 0.532 | 0.358 | 0.458 |
| 59.3 | 0.406 | 0.290 | 0.619 | 0.379 | 0.583 | 0.620 |
| 59.6 | 0.466 | 0.236 | 0.667 | 0.313 | 0.664 | 0.681 |
| 60.5 | 0.546 | 0.118 | 0.796 | 0.168 | 0.823 | 0.826 |
| 60.1 | 0.591 | 0.070 | 0.836 | 0.088 | 0.894 | 0.905 |
| 73.4 | 0.019 | 0.323 | 0.117 | 0.883 | 0.056 | 0.117 |
| 68.9 | 0.074 | 0.275 | 0.352 | 0.641 | 0.212 | 0.354 |
| 64.6 | 0.196 | 0.175 | 0.644 | 0.344 | 0.528 | 0.652 |
| 63.6 | 0.266 | 0.110 | 0.771 | 0.212 | 0.707 | 0.784 |
| 63.7 | 0.302 | 0.073 | 0.840 | 0.136 | 0.805 | 0.861 |
| 93.7 | 0.014 | 0.129 | 0.212 | 0.760 | 0.098 | 0.218 |
| 89.0 | 0.038 | 0.107 | 0.428 | 0.557 | 0.262 | 0.434 |
| . . . | 0.074 | 0.086 | 0.648 | 0.350 | 0.462 | 0.649 |
| 88.2 | 0.073 | 0.035 | 0.815 | 0.174 | 0.676 | 0.824 |
| System: 2,4-DMP$_1$–Benzene$_2$–Aniline$_3$ | | | | | | |
| 60.7 | 0.117 | 0.798 | 0.210 | 0.790 | 0.128 | 0.210 |
| 59.4 | 0.290 | 0.621 | 0.388 | 0.612 | 0.318 | 0.388 |
| 59.3 | 0.453 | 0.466 | 0.519 | 0.473 | 0.493 | 0.523 |
| 59.5 | 0.568 | 0.354 | 0.616 | 0.384 | 0.616 | 0.616 |
| 60.1 | 0.658 | 0.239 | 0.711 | 0.271 | 0.734 | 0.724 |
| 61.0 | 0.796 | 0.122 | 0.834 | 0.141 | 0.867 | 0.855 |
| 64.3 | 0.082 | 0.640 | 0.237 | 0.747 | 0.113 | 0.241 |
| 62.2 | 0.210 | 0.528 | 0.432 | 0.566 | 0.284 | 0.432 |
| 61.7 | 0.331 | 0.394 | 0.567 | 0.430 | 0.456 | 0.569 |
| 61.8 | 0.451 | 0.276 | 0.702 | 0.298 | 0.620 | 0.702 |
| 62.0 | 0.545 | 0.190 | 0.785 | 0.215 | 0.740 | 0.785 |
| 73.0 | 0.031 | 0.410 | 0.224 | 0.776 | 0.070 | 0.224 |
| 67.4 | 0.090 | 0.338 | 0.470 | 0.488 | 0.210 | 0.491 |
| 64.9 | 0.159 | 0.272 | 0.616 | 0.348 | 0.368 | 0.639 |
| 63.2 | 0.259 | 0.195 | 0.756 | 0.233 | 0.570 | 0.765 |
| 63.0 | 0.356 | 0.089 | 0.868 | 0.126 | 0.799 | 0.882 |
| 81.3 | 0.020 | 0.258 | 0.264 | 0.708 | 0.072 | 0.272 |
| 73.0 | 0.063 | 0.169 | 0.637 | 0.343 | 0.272 | 0.650 |
| 66.0 | 0.116 | 0.134 | 0.776 | 0.217 | 0.462 | 0.781 |
| 63.1 | 0.215 | 0.056 | 0.923 | 0.071 | 0.794 | 0.929 |
| System: 2,4-DMP$_1$–Benzene$_2$–Furfural$_3$ | | | | | | |
| 60.2 | 0.115 | 0.811 | 0.200 | 0.800 | 0.124 | 0.200 |
| 59.2 | 0.290 | 0.628 | 0.393 | 0.607 | 0.316 | 0.393 |
| 59.0 | 0.431 | 0.472 | 0.518 | 0.482 | 0.477 | 0.518 |
| 58.9 | 0.559 | 0.365 | 0.615 | 0.385 | 0.605 | 0.615 |
| 59.6 | 0.663 | 0.245 | 0.702 | 0.286 | 0.730 | 0.711 |
| 60.7 | 0.781 | 0.121 | 0.810 | 0.150 | 0.865 | 0.844 |
| 63.9 | 0.072 | 0.656 | 0.216 | 0.780 | 0.099 | 0.217 |
| 61.1 | 0.212 | 0.520 | 0.438 | 0.556 | 0.290 | 0.440 |
| 60.6 | 0.330 | 0.392 | 0.562 | 0.434 | 0.457 | 0.565 |
| 60.6 | 0.465 | 0.291 | 0.685 | 0.306 | 0.615 | 0.691 |
| 60.8 | 0.541 | 0.198 | 0.762 | 0.226 | 0.732 | 0.771 |
| 61.2 | 0.660 | 0.089 | 0.887 | 0.099 | 0.881 | 0.900 |
| 70.5 | 0.031 | 0.424 | 0.224 | 0.744 | 0.068 | 0.231 |
| 65.1 | 0.100 | 0.369 | 0.472 | 0.494 | 0.213 | 0.489 |
| 61.9 | 0.192 | 0.294 | 0.633 | 0.352 | 0.395 | 0.643 |
| . . . | 0.298 | 0.173 | 0.763 | 0.209 | 0.634 | 0.785 |
| 76.1 | 0.021 | 0.334 | 0.208 | 0.746 | 0.059 | 0.218 |
| 72.6 | 0.038 | 0.332 | 0.340 | 0.611 | 0.103 | 0.358 |
| 69.3 | 0.059 | 0.292 | 0.469 | 0.503 | 0.168 | 0.482 |
| 64.1 | 0.127 | 0.240 | 0.669 | 0.300 | 0.346 | 0.690 |

Table VII. Empirical Constants *a* and *b* for the Ternary System Correlation

| The Binary System Plus | *a* | *b* |
|---|---|---|
| Hexylene glycol | 0.210 | −0.170 |
| Aniline | 0.580 | −0.370 |
| Furfural | 0.433 | −0.484 |

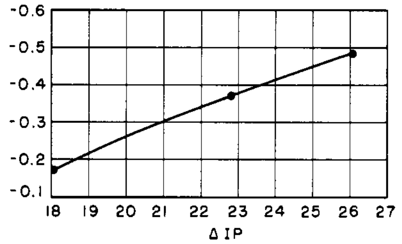

Figure 13. Empirical constant "b" is a function of internal pressure difference between solvent and 2,4-DMP

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# Heat Content of Platinum

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CHEMICAL INERTNESS, high melting point, and freedom from allotropic and magnetic transformations give platinum obvious advantages as a secondary standard for calibrating high-temperature calorimeters. However, currently accepted tables (*8, 13*) of the heat content of platinum can be criticized because the values below 500° K. are too high to join smoothly with reliable low-temperature (< 298° K.) heat capacity data (*1, 12*), and because the tables are based mainly on the drop calorimetry of Jaeger and others (*4, 5, 6*) in which, as Oriani (*10*) has pointed out, the heat lost by the sample during the drop was not properly taken into account.

The performance of a diphenyl ether calorimeter used in this laboratory is routinely checked by dropping samples of platinum. The results so obtained scatter considerably more than those by Jaeger and others (*4, 5, 6*) from larger samples, but they do show clearly that the over-all systematic error in Jaeger's work is very small. They also show the previously tabulated heat contents at 400° and 500° K. are somewhat too high.

## EXPERIMENTAL

Since the diphenyl ether calorimeter has been described previously (*3*), the procedure and sample preparation will be described here only briefly.

Four samples, each about 99.99% pure, were used in the determinations. The first was a solid sphere about 8 mm. in diameter weighing 5.6 grams. The second was formed from 0.7 gram of 0.127 mm. platinum foil to make a hollow sphere of the same diameter as the first. The third and fourth samples were similar to the second, except that they were filled with 1.9 grams of platinum wire and 1.1 grams of platinum foil, respectively.

The samples were heated under an argon atmosphere in a resistance furnace to a measured temperature, *T*, then dropped into the diphenyl ether calorimeter. The heat liberated by a sample within the calorimeter is absorbed by a mixture of liquid plus solid diphenyl ether, melting some of the solid without changing its temperature. The expansion accompanying melting forces mercury from a pool in