the LiCl-KCl system *(8)* indicate that the slight difference in composition between our melt and that of Jaeger's (42 mol % KCl vs. 40.5 mol % KCl) would result in a change in surface tension of less than 0.5%.

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# Thermodynamic Properties of Neopentane

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**The effect of pressure on the enthalpy and entropy of 2,2-dimethylpropane (neopentane) was evaluated numerically from experimental *PVT* data. The resulting values were used in conjunction with ideal state properties from the literature to construct the Mollier diagram for the temperature range of 620–900°R and for pressures up to 4500 psia.**

The development of the fundamental equations employed in the evaluation ot the enthalpy and entropy were presented by Hsu and McKetta (*3*). These relationships, Equations 1–6, use the volume residual concept:

$$\Delta H_{P,T} = \Delta H_T^\circ + H_P + (\Delta H_v)_{T_0} \tag{1}$$

$$\Delta S_{P,T} = \Delta S_T^\circ + S_P + (\Delta S_v)_{T_0} \tag{2}$$

$$\Delta H_T^\circ = \int_{T_0}^{T} C_P^\circ \, dT \tag{3}$$

$$\Delta S_T^\circ = \int_{T_0}^{T} \frac{C_P^\circ}{T} \, dT \tag{4}$$

$$H_P = J\left\{ \int_0^P \left[T\left(\frac{\partial \gamma}{\partial T}\right)_P - \gamma\right]_T dP - \int_0^{P_0} \left[T\left(\frac{\partial \gamma}{\partial T}\right)_P - \gamma\right]_{T_0} dP \right\} \tag{5}$$

$$S_P = J \int_0^P \left[\left(\frac{\partial \gamma}{\partial T}\right)_P\right]_T dP - R \ln (P/P_0) - J \int_0^{P_0} \left[\left(\frac{\partial \gamma}{\partial T}\right)_P\right]_{T_0} dP \tag{6}$$

The experimental *PVT* data (*2*) were smoothed and interpolated by the least-squares method of Lin (*4*) into an evenly spaced array of pressure, temperature, and volume residual. Values were selected from regions of this array to evaluate constants in a localized equation of state,

$$\gamma = C_1 + C_2P + C_3P^2 + C_4T + C_5PT + C_6P^2T + C_7T^2 + C_8PT^2 + C_9P^2T^2 \tag{7}$$

which was used analytically in Equations 5 and 6 to evaluate the derivatives and the pressure integrals by integration over subintervals with 5 psi increments. Details of these calculations were presented by Lin (*4, 5*).

The change in fugacity coefficient for each pressure increment was evaluated by substituting Equation 7 into:

$$\nu_2 = \nu_1 \exp\left(\frac{-1}{RT} \int_{P_1}^{P_2} \gamma \, dP\right) \tag{8}$$

Specific volumes were similarly found by using Equation 7 in the following definition of the volume residual:

$$V = RT/P - \gamma(T,P) \tag{9}$$

### Reference State

The saturated liquid at 620°R was taken as the reference state—i.e., $\Delta H_{P,T} = 0$ and $\Delta S_{P,T} = 0$, for evaluation of the enthalpies and entropies presented here. The vapor pressure of neopentane at this temperature was 87.61 psia as calculated from the Nernst equation reported by Dawson et al. (*2*).

### Sources of Data

The experimental volumetric data used to evaluate the enthalpies and entropies presented here were taken from the work of Dawson et al. (*1, 2*). Saturated state densities, heats of vaporization, and vapor pressures were calculated from correlations in the same work.

The isobaric integrations required in Equations 3 and 4 were performed at zero pressure using the ideal state heat capacities reported by Pitzer and Kilpatrick (*6*). To allow analytical integration, the equation of Yuan and Mok (*7*) was used,

$$C_p^\circ = 15.4496 + 92.6474 \exp(-571.7382/T) \tag{10}$$

where *T* is the temperature, K. The constants in Equation 10 were evaluated by an iterative least-squares method using the data of Pitzer and Kilpatrick. The standard error of the regression was 0.088 Btu/lb °R and the average absolute deviation was 0.035 Btu/lb °R. Furthermore, the maximum deviation of reported heat capacity data from those calculated by Equation 10 was less than the error in the original data. This equation was substituted into Equations 3 and 4, and the integrations were performed

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analytically to evaluate the ideal state changes in enthalpy and entropy. Comparison of these calculated entropies and literature values (*6*) showed a maximum deviation of 0.0003 Btu/lb °R.

### Thermodynamic Properties and Mollier Diagram

Representative values of enthalpy, entropy, fugacity coefficients, and specific volumes in the gaseous state as calculated by the methods described above are presented in Table I. (A complete table of values at 10°R increments is available from the ACS Microfilm Depository Service.)

Saturated vapor state properties were calculated by integrating Equations 5 and 6 to the vapor pressure at each temperature. These values and the enthalpy and entropy of vaporization from the previous work (*2*) were used to calculate the properties of the saturated liquid. Saturated state densities were also taken from the work of Dawson et al. (*2*). These thermodynamic properties for neopentane are presented in Table II.

The Mollier diagram (Figure 1) was constructed from the values of enthalpy and entropy in Tables I and II.

### Discussion

The internal consistency of the values in Table I was tested by using the equation

$$(\partial H/\partial S)_P = T \qquad (11)$$

which can be integrated isobarically to yield

$$\left[H_2 - H_1 = T_2S_2 - T_1S_1 - \int_{T_1}^{T_2} S dT\right]_P \qquad (12)$$

The equality in Equation 12 was tested for six isobars. The integral in Equation 12 was evaluated by both trapezoidal and Simpson's rules with no significant differences found. Table III shows that the maximum deviation was less than 0.1 Btu/lb.

Based on the precision indicated in Table III and the accuracy of the experimental *PVT* data, the enthalpy data reported here are believed to be correct to within ±0.08 Btu/lb and the entropy to within ±0.0005 Btu/lb °R.

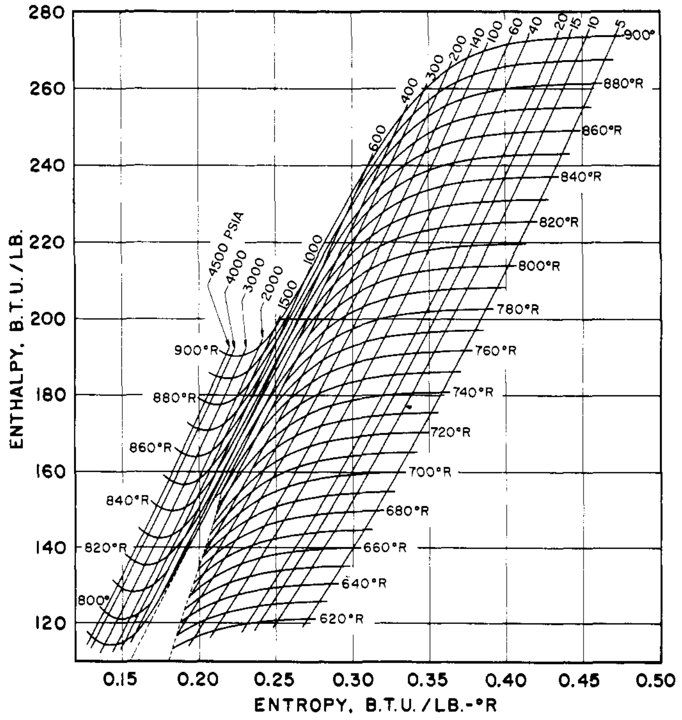

**Figure 1.** Mollier diagram for neopentane

**Table I (Abridged). Thermodynamic Properties of Gaseous Neopentane**

Reference state: *H* = 0 and *S* = 0 for the saturated liquid at 620°R and 87.61 psia

*T* = temperature, °R
*P* = pressure, psia
*V* = volume, ft³/lb
*H* = enthalpy, Btu/lb
*S* = entropy, Btu/lb °R
$\nu$ = fugacity coefficient

| *T* | *P* | *V* | *H* | *S* | $\nu$ |
|---|---|---|---|---|---|
| 620 | 5 | 18.30 | 121.1 | 0.2705 | 0.9924 |
| | 10 | 9.079 | 120.7 | 0.2509 | 0.9848 |
| | 15 | 6.004 | 120.3 | 0.2393 | 0.9772 |
| | 20 | 4.466 | 119.8 | 0.2309 | 0.9696 |
| | 25 | 3.543 | 119.4 | 0.2242 | 0.9620 |
| | 30 | 2.927 | 118.9 | 0.2187 | 0.9544 |
| | 35 | 2.486 | 118.5 | 0.2139 | 0.9468 |
| | 40 | 2.156 | 118.0 | 0.2097 | 0.9391 |
| | 50 | 1.692 | 117.1 | 0.2025 | 0.9239 |
| | 60 | 1.382 | 116.1 | 0.1963 | 0.9087 |
| | 70 | 1.160 | 115.1 | 0.1909 | 0.8935 |
| | 80 | 0.9907 | 114.0 | 0.1860 | 0.8781 |
| 900 | 10 | 13.33 | 273.5 | 0.4524 | 0.9955 |
| | 20 | 6.632 | 273.1 | 0.4330 | 0.9910 |
| | 40 | 3.286 | 272.4 | 0.4133 | 0.9820 |
| | 60 | 2.170 | 271.7 | 0.4016 | 0.9730 |
| | 80 | 1.612 | 270.9 | 0.3931 | 0.9642 |
| | 100 | 1.277 | 270.0 | 0.3862 | 0.9554 |
| | 150 | 0.8302 | 267.6 | 0.3730 | 0.9336 |
| | 200 | 0.6062 | 265.0 | 0.3629 | 0.9120 |
| | 250 | 0.4714 | 262.2 | 0.3543 | 0.8906 |
| | 300 | 0.3812 | 259.3 | 0.3467 | 0.8694 |
| | 350 | 0.3168 | 256.0 | 0.3394 | 0.8485 |
| | 400 | 0.2687 | 251.9 | 0.3318 | 0.8278 |
| | 450 | 0.2293 | 249.2 | 0.3263 | 0.8070 |
| | 500 | 0.1996 | 246.3 | 0.3208 | 0.7870 |
| | 550 | 0.1741 | 243.1 | 0.3154 | 0.7672 |
| | 600 | 0.1528 | 239.8 | 0.3100 | 0.7476 |
| | 650 | 0.1346 | 236.2 | 0.3046 | 0.7282 |
| | 700 | 0.1191 | 232.5 | 0.2992 | 0.7090 |
| | 750 | 0.1058 | 228.6 | 0.2937 | 0.6901 |
| | 800 | 0.09455 | 224.7 | 0.2884 | 0.6717 |
| | 850 | 0.08524 | 220.9 | 0.2832 | 0.6537 |
| | 900 | 0.07767 | 217.3 | 0.2784 | 0.6365 |
| | 950 | 0.07160 | 214.1 | 0.2740 | 0.6200 |
| | 1000 | 0.06675 | 211.2 | 0.2701 | 0.6045 |
| | 1100 | 0.05960 | 206.5 | 0.2636 | 0.5760 |
| | 1200 | 0.05498 | 203.2 | 0.2587 | 0.5510 |
| | 1300 | 0.05176 | 200.7 | 0.2549 | 0.5293 |
| | 1400 | 0.04940 | 198.8 | 0.2517 | 0.5104 |
| | 1500 | 0.04759 | 197.2 | 0.2490 | 0.4939 |
| | 1600 | 0.04613 | 196.0 | 0.2466 | 0.4795 |
| | 1800 | 0.04385 | 194.0 | 0.2426 | 0.4558 |
| | 2000 | 0.04230 | 192.5 | 0.2391 | 0.4375 |
| | 2200 | 0.04086 | 191.5 | 0.2363 | 0.4232 |
| | 2400 | 0.03996 | 190.6 | 0.2336 | 0.4121 |
| | 2600 | 0.03906 | 190.4 | 0.2318 | 0.4035 |
| | 2800 | 0.03832 | 190.2 | 0.2300 | 0.3970 |
| | 3000 | 0.03766 | 190.1 | 0.2284 | 0.3921 |
| | 3200 | 0.03711 | 190.0 | 0.2266 | 0.3887 |
| | 3400 | 0.03550 | 189.9 | 0.2250 | 0.3866 |
| | 3600 | 0.03613 | 189.9 | 0.2235 | 0.3855 |
| | 3800 | 0.03572 | 189.9 | 0.2221 | 0.3853 |
| | 4000 | 0.03534 | 190.0 | 0.2208 | 0.3860 |
| | 4200 | 0.03499 | 190.2 | 0.2194 | 0.3875 |
| | 4400 | 0.03465 | 190.3 | 0.2182 | 0.3896 |
| | 4500 | 0.03450 | 190.4 | 0.2176 | 0.3909 |

**Table II. Thermodynamic Properties of Saturated Neopentane**

| | | Vol, $ft^3/lb$ | | Enthalpy, Btu/lb | | | Entropy, Btu/lb °R | | | $\nu$, |
|---|---|---|---|---|---|---|---|---|---|---|
| Temp, °R | Press, psia | Satd liquid | Satd vapor | Satd liquid | Vaporization | Satd vapor | Satd liquid | Vaporization | Satd vapor | fugacity coefficient |
| 620 | 87.61 | 0.03041 | 0.8694 | 0 | 113.06 | 113.06 | 0 | 0.1823 | 0.1823 | 0.8663 |
| 625 | 93.41 | 0.03063 | 0.8215 | 4.48 | 110.33 | 114.81 | 0.0072 | 0.1765 | 0.1837 | 0.8610 |
| 630 | 99.49 | 0.03084 | 0.7754 | 7.58 | 108.90 | 116.48 | 0.0120 | 0.1728 | 0.1848 | 0.8548 |
| 635 | 105.86 | 0.03107 | 0.7313 | 10.84 | 107.44 | 118.28 | 0.0172 | 0.1692 | 0.1864 | 0.8500 |
| 640 | 112.52 | 0.03131 | 0.6892 | 14.07 | 105.95 | 120.01 | 0.0220 | 0.1656 | 0.1876 | 0.8445 |
| 645 | 119.49 | 0.03156 | 0.6492 | 17.23 | 104.43 | 121.66 | 0.0269 | 0.1619 | 0.1888 | 0.8382 |
| 650 | 126.76 | 0.03181 | 0.6112 | 20.56 | 102.89 | 123.45 | 0.0321 | 0.1583 | 0.1904 | 0.8336 |
| 655 | 134.36 | 0.03208 | 0.5753 | 23.81 | 101.30 | 125.11 | 0.0368 | 0.1547 | 0.1915 | 0.8269 |
| 660 | 142.27 | 0.03236 | 0.5414 | 27.22 | 99.69 | 126.91 | 0.0421 | 0.1510 | 0.1931 | 0.8220 |
| 665 | 150.52 | 0.03265 | 0.5094 | 30.59 | 98.03 | 128.62 | 0.0471 | 0.1474 | 0.1945 | 0.8162 |
| 670 | 159.12 | 0.03296 | 0.4793 | 33.87 | 96.34 | 130.21 | 0.0518 | 0.1438 | 0.1956 | 0.8094 |
| 675 | 168.08 | 0.03327 | 0.4509 | 37.42 | 94.60 | 132.02 | 0.0571 | 0.1402 | 0.1973 | 0.8046 |
| 680 | 177.41 | 0.03361 | 0.4241 | 40.87 | 92.81 | 133.68 | 0.0621 | 0.1365 | 0.1986 | 0.7987 |
| 685 | 187.10 | 0.03396 | 0.3989 | 44.37 | 90.97 | 135.34 | 0.0671 | 0.1328 | 0.1999 | 0.7926 |
| 690 | 197.22 | 0.03433 | 0.3751 | 47.90 | 89.07 | 136.97 | 0.0722 | 0.1291 | 0.2013 | 0.7864 |
| 695 | 207.70 | 0.03472 | 0.3528 | 51.47 | 87.12 | 138.59 | 0.0772 | 0.1254 | 0.2026 | 0.7805 |
| 700 | 218.64 | 0.03513 | 0.3317 | 55.07 | 85.09 | 140.16 | 0.0877 | 0.1216 | 0.2039 | 0.7743 |
| 705 | 229.93 | 0.03557 | 0.3118 | 58.69 | 82.99 | 141.68 | 0.0874 | 0.1177 | 0.2051 | 0.7680 |
| 710 | 241.70 | 0.03604 | 0.2929 | 62.38 | 80.80 | 143.18 | 0.0924 | 0.1138 | 0.2062 | 0.7618 |
| 715 | 253.85 | 0.03654 | 0.2751 | 66.11 | 78.52 | 144.63 | 0.0976 | 0.1098 | 0.2074 | 0.7555 |
| 720 | 266.49 | 0.03707 | 0.2582 | 69.89 | 76.14 | 146.03 | 0.1028 | 0.1057 | 0.2085 | 0.7491 |
| 725 | 279.59 | 0.03765 | 0.2422 | 73.68 | 73.63 | 147.31 | 0.1078 | 0.1016 | 0.2094 | 0.7422 |
| 730 | 293.18 | 0.03827 | 0.2270 | 77.73 | 70.99 | 148.72 | 0.1133 | 0.09724 | 0.2105 | 0.7361 |
| 735 | 307.26 | 0.03896 | 0.2124 | 81.78 | 68.18 | 149.96 | 0.1186 | 0.09276 | 0.2114 | 0.7295 |
| 740 | 321.89 | 0.03971 | 0.1984 | 85.86 | 65.18 | 151.04 | 0.1240 | 0.08808 | 0.2121 | 0.7228 |
| 745 | 337.04 | 0.04055 | 0.1850 | 90.10 | 61.95 | 152.05 | 0.1343 | 0.08315 | 0.2174 | 0.7160 |
| 750 | 352.76 | 0.04150 | 0.1720 | 94.54 | 58.42 | 152.96 | 0.1353 | 0.07790 | 0.2132 | 0.7093 |
| 755 | 369.08 | 0.04260 | 0.1593 | 98.94 | 54.53 | 153.47 | 0.1411 | 0.07223 | 0.2133 | 0.7015 |
| 760 | 385.97 | 0.04390 | 0.1467 | 103.99 | 50.15 | 154.14 | 0.1475 | 0.06598 | 0.2135 | 0.6953 |
| 765 | 403.51 | 0.04549 | 0.1341 | 109.65 | 45.05 | 154.70 | 0.1548 | 0.05889 | 0.2137 | 0.6878 |
| 770 | 421.70 | 0.04758 | 0.1209 | 115.31 | 38.84 | 154.15 | 0.1620 | 0.05044 | 0.2124 | 0.6808 |
| 775 | 440.63 | 0.05071 | 0.1063 | 123.07 | 30.45 | 153.52 | 0.1717 | 0.03929 | 0.2110 | 0.6736 |
| 780 | 460.13 | 0.05853 | 0.08411 | 138.82 | 13.77 | 152.59 | 0.1917 | 0.01766 | 0.2094 | 0.6661 |

**Table III. Internal Consistency Check**

| | | $\Delta H$, Btu/lb | | |
|---|---|---|---|---|
| Press., psia | Temp range, °R | Table I | Eq 12 | Dev. |
| 60 | 620–900 | 155.6 | 155.58 | 0.02 |
| 300 | 740–900 | 104.4 | 104.49 | −0.09 |
| 1000 | 790–900 | 94.0 | 94.02 | −0.02 |
| 2000 | 790–900 | 78.0 | 77.97 | 0.03 |
| 3000 | 790–900 | 75.8 | 75.84 | −0.04 |
| 4500 | 790–900 | 73.9 | 73.99 | −0.09 |

## Nomenclature

$C_P°$ = ideal state heat capacity at constant pressure, Btu/lb °R

$f$ = fugacity

$\Delta H_{P,T}$ = enthalpy at $P$, $T$ above the saturated liquid state at $P_0$, $T_0$, Btu/lb

$\Delta H_T°$ = change of enthalpy in ideal state from $T_0$ to $T$, Btu/lb

$(\Delta H_v)_{T_0}$ = heat of vaporization at the reference temperature, $T_0$, Btu/lb

$J$ = dimensional constant for neopentane, 0.00256644 (Btu/lb) $(ft^3/lb\ mol)^{-1}$ $(psia)^{-1}$

$P$ = pressure, psia

$P_0$ = reference pressure, psia

$R$ = gas constant for neopentane, 0.14874 (psi) $(ft^3)$/(°R) (lb), 0.027542 (Btu)/(°R) (lb)

$\Delta S_{P,T}$ = entropy at $P$, $T$ above the saturated liquid state at $P_0$, $T_0$, Btu/lb °R

$\Delta S_T°$ = change of entropy in ideal state from $T_0$ to $T$, Btu/lb °R

$(\Delta S_v)_{T_0}$ = entropy of vaporization at the reference temperature, $T_0$, Btu/lb °R

$T$ = temperature, °R

$T_0$ = reference temperature, 620°R

$V$ = specific volume, $ft^3/lb$

$\gamma$ = volume residual, $(RT/P) - V$, $ft^3/lb$

$\nu$ = fugacity coefficient, $f/P$

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