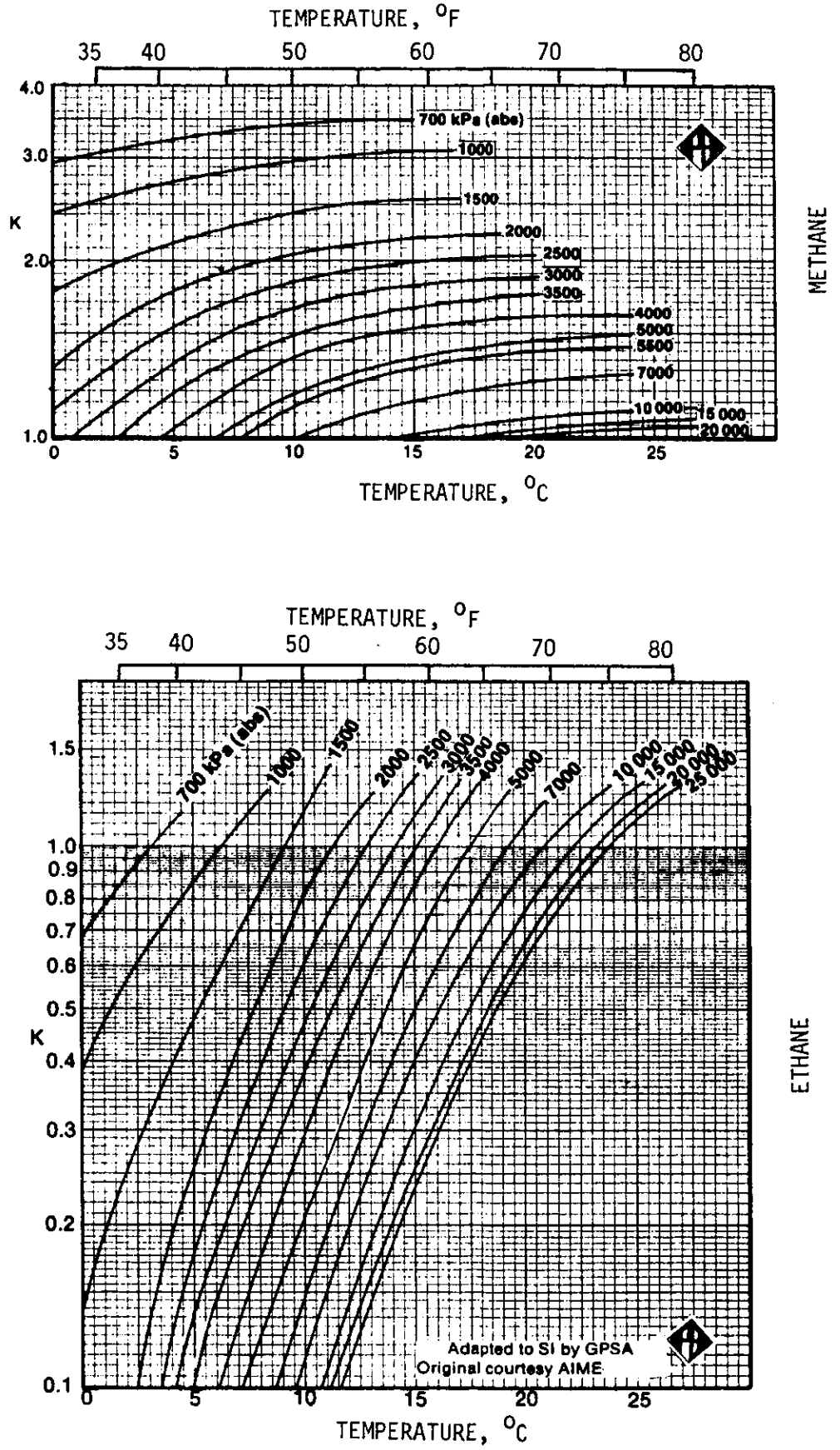


**Figure 6.14 Vapor-Solid K Values for Methane and Ethane**

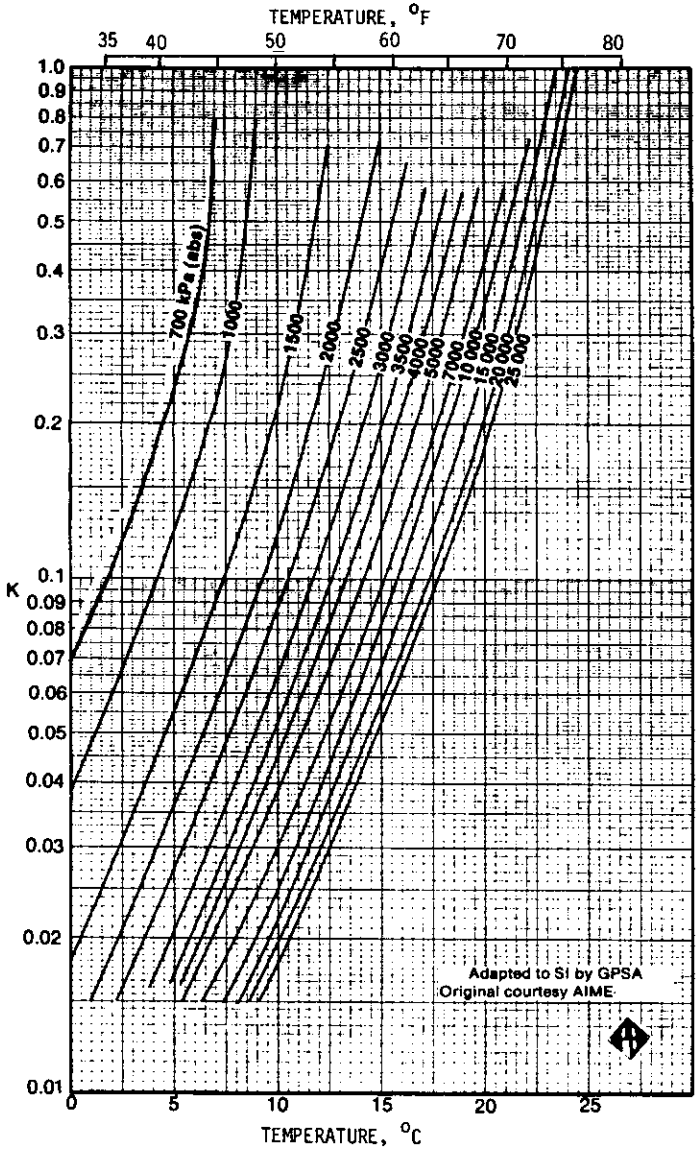


**Figure 6.15 Vapor-Solid K Values for Propane**

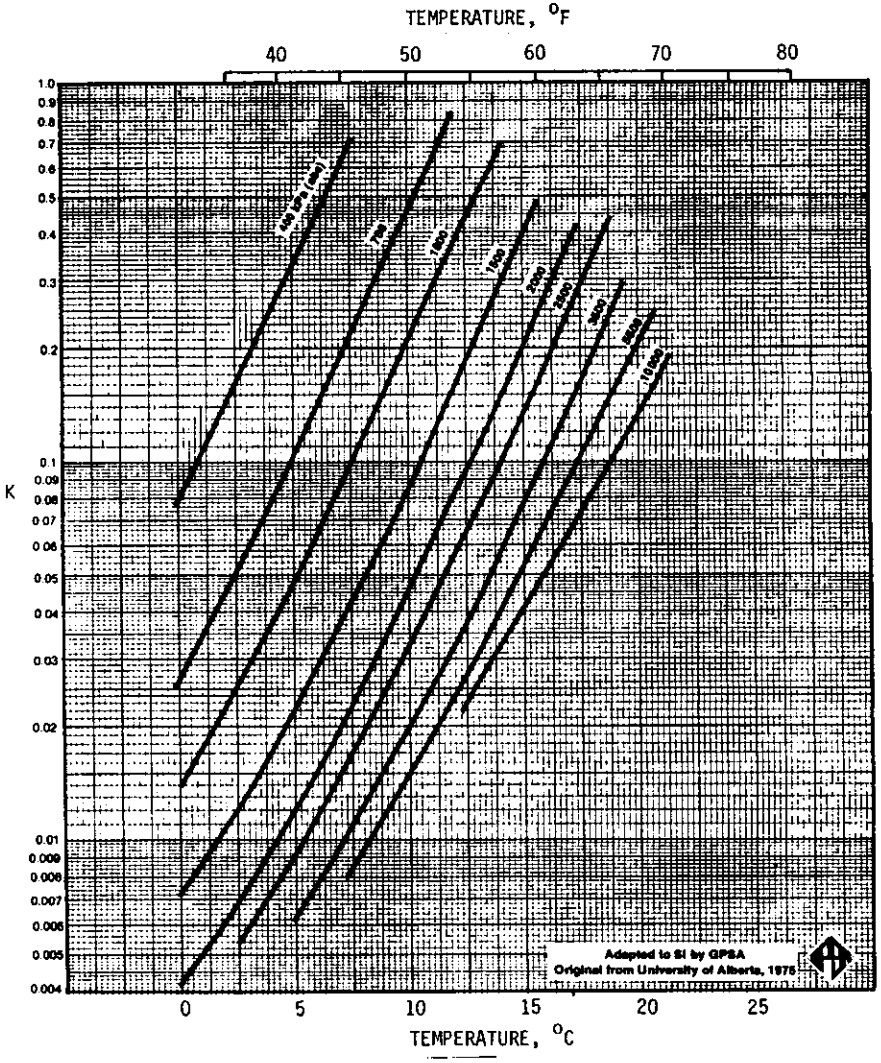


**Figure 6.16 Vapor-Solid K Values for iso-Butane**

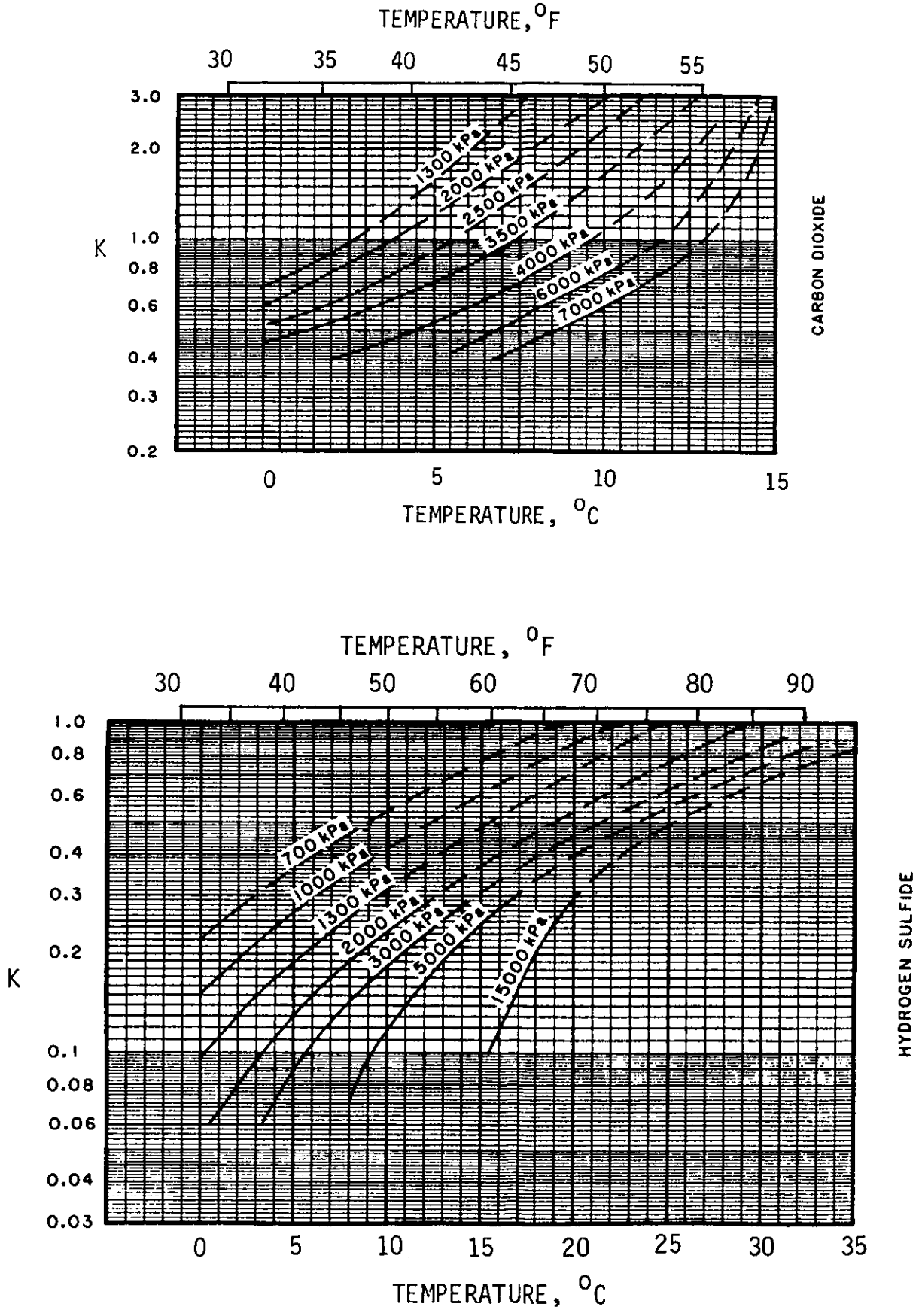


**Figure 6.17 Vapor-Solid K Values for $CO_2$ and $H_2S$**

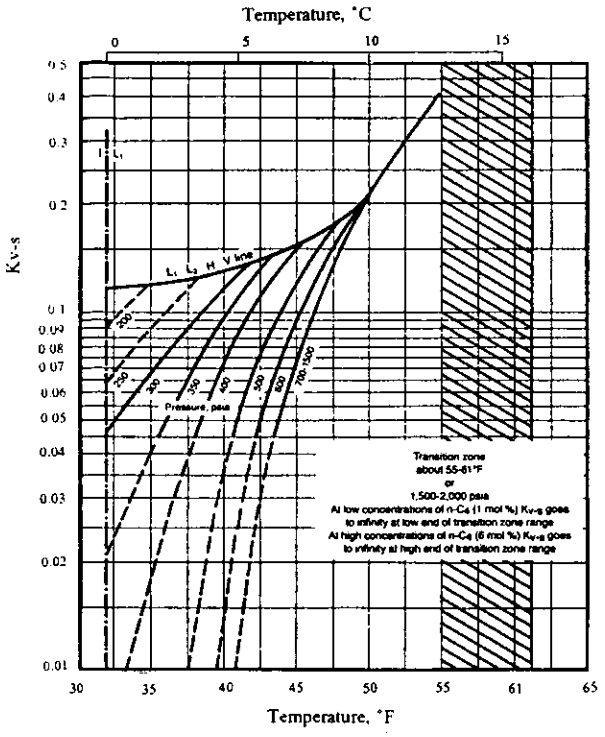


**Figure 6.18 Vapor-Solid Equilibrium Constants for n-Butane**

A dewpoint type calculation is made using the $K_{v-s}$ values shown. The term "$y_i$" is the mol fraction of each component in the gas. $K_{v-s}$ equals infinity for all nonhydrate formers present.

$$\sum(y_i/K_{v-s}) = 1.0 \tag{6.5}$$

**Example 6.3:** Find the hydrate formation temperature of the gas below at 2.0 MPa [290 psia].

| Component | $y_i$ | At 10°C [50°F] | |
|---|---|---|---|
| | | $K_{v-s}$ | $y_i/K_{v-s}$ |
| Nitrogen | 0.094 | Inf | 0.0 |
| Methane | 0.784 | 2.04 | 0.384 |
| Ethane | 0.060 | 0.82 | 0.073 |
| Propane | 0.036 | 0.113 | 0.319 |
| Iso-Butane | 0.005 | 0.047 | 0.106 |
| n-Butane | 0.019 | 0.21 | 0.090 |
| $CO_2$ | 0.002 | 2.9 | 0.001 |
| | 1.000 | | 0.974 |

One can assume a new temperature and repeat the calculation. In Example 6.3 the result will be a hydrate formation temperature of about 9.5°C [49°F].

The preceding approach may also be applied using a different set of $K_{v-s}$ values. Sloan *et al.*[6.20] present $K_{v-s}$ values which are dependent upon composition and type of hydrate structure (I or II).

## Trekell-Campbell Method

The Katz method possesses pressure limitations and fails to address the hydrate depression effects of molecules too large to fit into the cavities. Too many of these in one location makes it difficult for a stable lattice to form around them.

The molecules larger than methane increase the ease of stable hydrate formation. This method[6.21] uses methane as the reference condition. The additive effect of other molecules is then plotted in Figures 6.19-6.21 for a pressure range 6.9-41.4 MPa [1000-6000 psia]. Each figure is for a specific pressure and the corresponding methane hydrate forming temperature. The abscissa shows the displacement of this methane hydrate forming temperature for the percentage of each component shown on the ordinate.

Notice in Figure 6.19 that n-butane has a slightly positive effect on hydrate formation. In Figures 6.20 and 6.21 the temperature displacement is negative (n-butane becomes a nonhydrate former). This change probably is due to distortion of the lattice with pressure which does not allow even the largest cavities to hold a molecule as large as n-butane.

Figure 6.22 is the negative correction (depression) for nonhydrate formers (pentanes plus). The key parameter is

$$\frac{y_{C_5+}}{1 - y_{C_1} - y_{C_5+}} (100)$$

or the ratio of the mol fraction of pentanes plus to the sum of the mol fractions ethane, propane and butanes. Increasing this ratio is unfavorable to hydrate formation; there are too many large molecules present.

The following general procedure is recommended for this method:

1. Calculate the hydrocarbon dewpoint curve to locate line FEGC in Figure 6.13.
2. Using the 6.9 MPa prediction chart, determine the hydrate formation temperature by algebraically summing temperature displacements. Use the dry gas analysis for the ordinate values and sum the $\Delta T$ values found on the abscissa to the temperature for methane hydrate given on the figure. Correct this temperature for the effect of pentanes and heavier if present.
3. Repeat the previous step at 13.8 MPa and correct for pentanes and heavier.
4. Calculate the hydrate temperature at each remaining pressure for which there is a graph until the hydrocarbon dewpoint pressure is reached.
5. Plot the calculated temperatures and fit the best curve through the points.

The procedure shows that pentane and heavier have a calculable effect on hydrate point, and the "K" value is not infinity.

Limited data show that $H_2S$ and $CO_2$ elevate the hydrate point less in natural gases containing reasonable amounts of ethanes through propanes than would be expected from their binary data with methane. In fact, the correction for $CO_2$ is negligible for most gases tested. In the final analysis, one does not need an exact hydrate forming prediction. A narrow range of 1-2°C is suitable for design and operation.

I do not recommend that you extrapolate the curves in Figure 6.19-6.22. At some composition the lines approach the vertical (infinite slope) and any increase in concentration produces no further temperature deflection. But, one also must remember that the correlation is empirical and that any extrapolation tends to increase the risk.

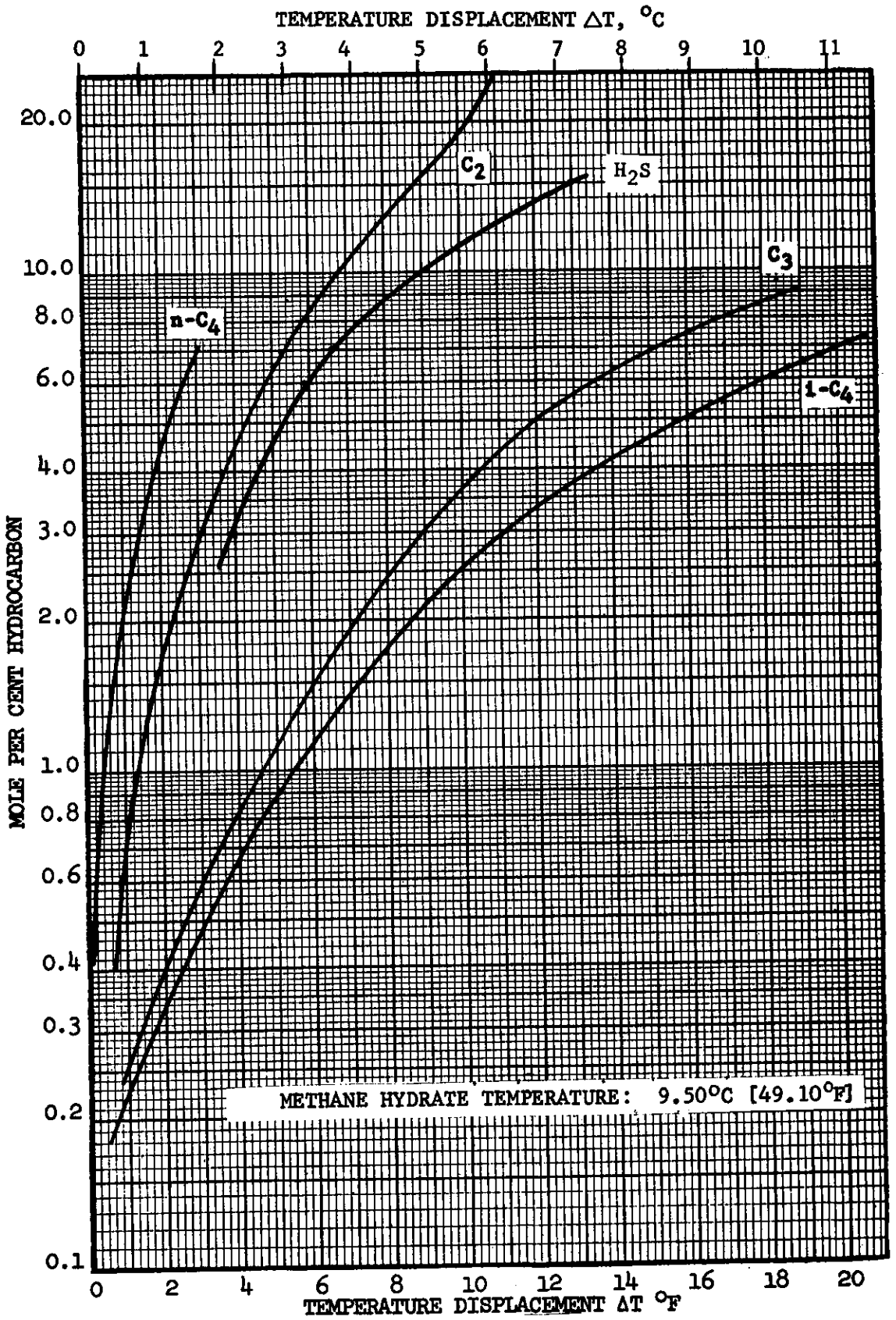


**Figure 6.19 Hydrate Prediction Correlations at 6.9 MPa**

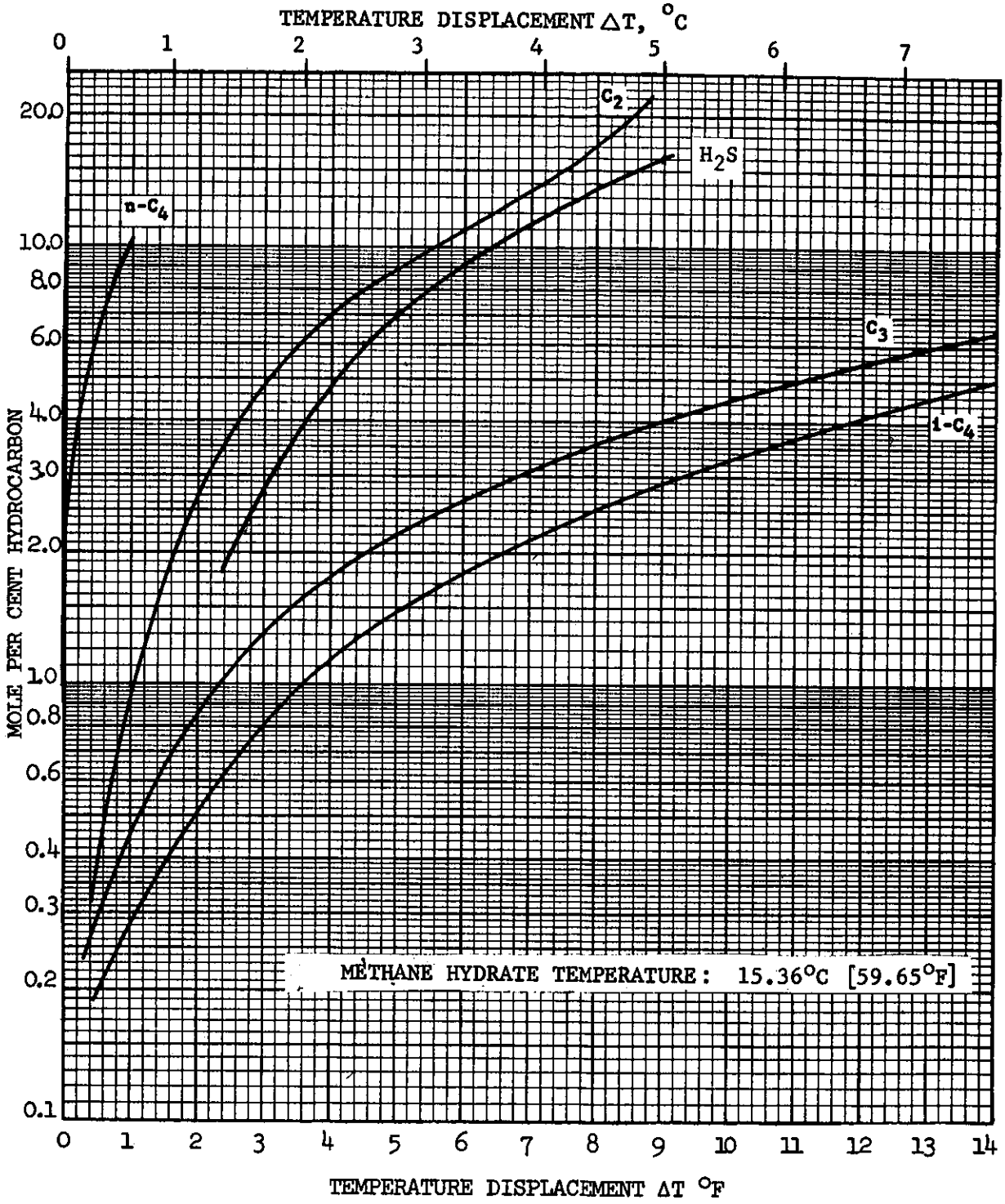


Figure 6.19(a) Hydrate Prediction Correlations at 13.8 MPa

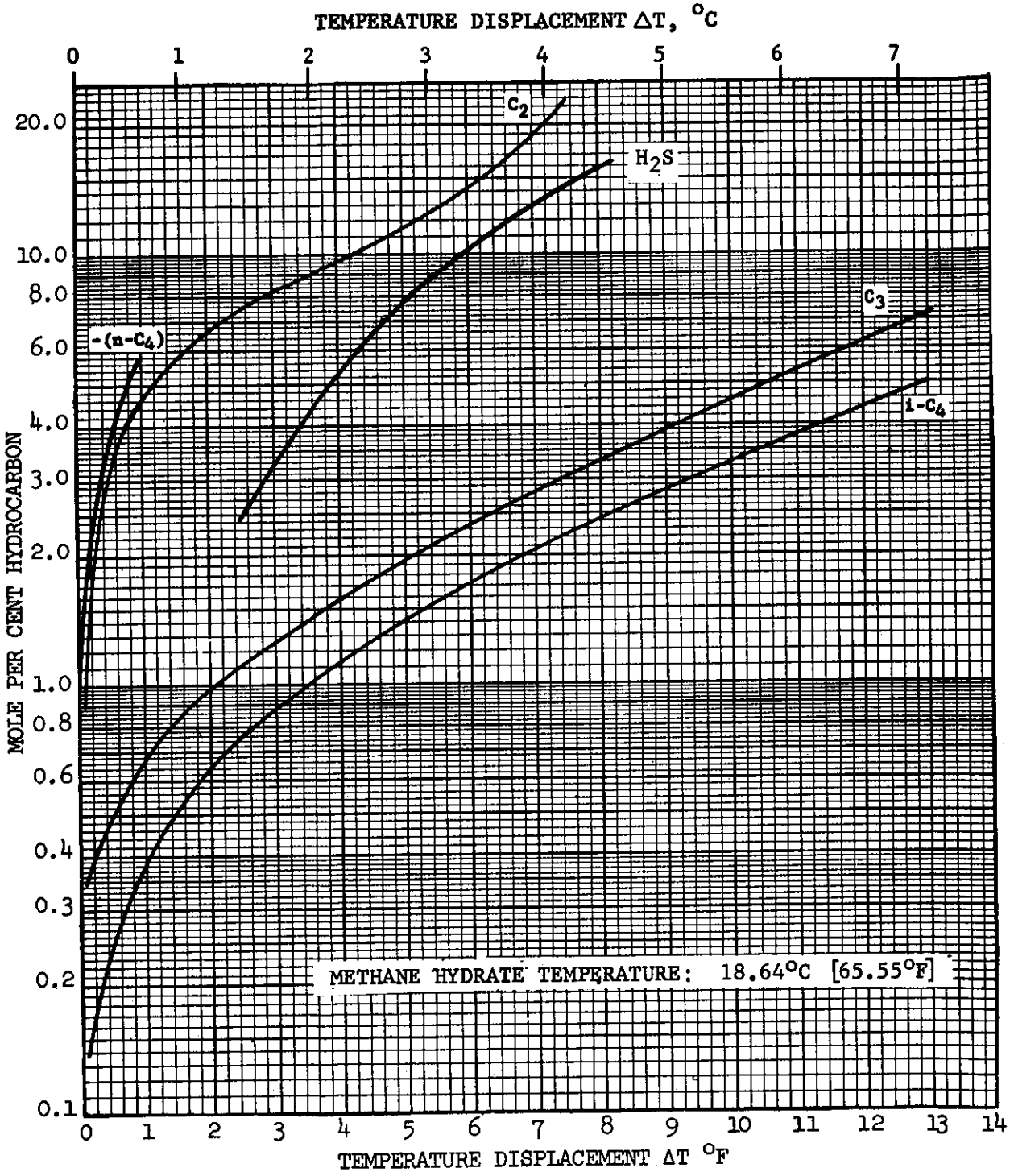


**Figure 6.20 Hydrate Prediction Correlations at 20.7 MPa**

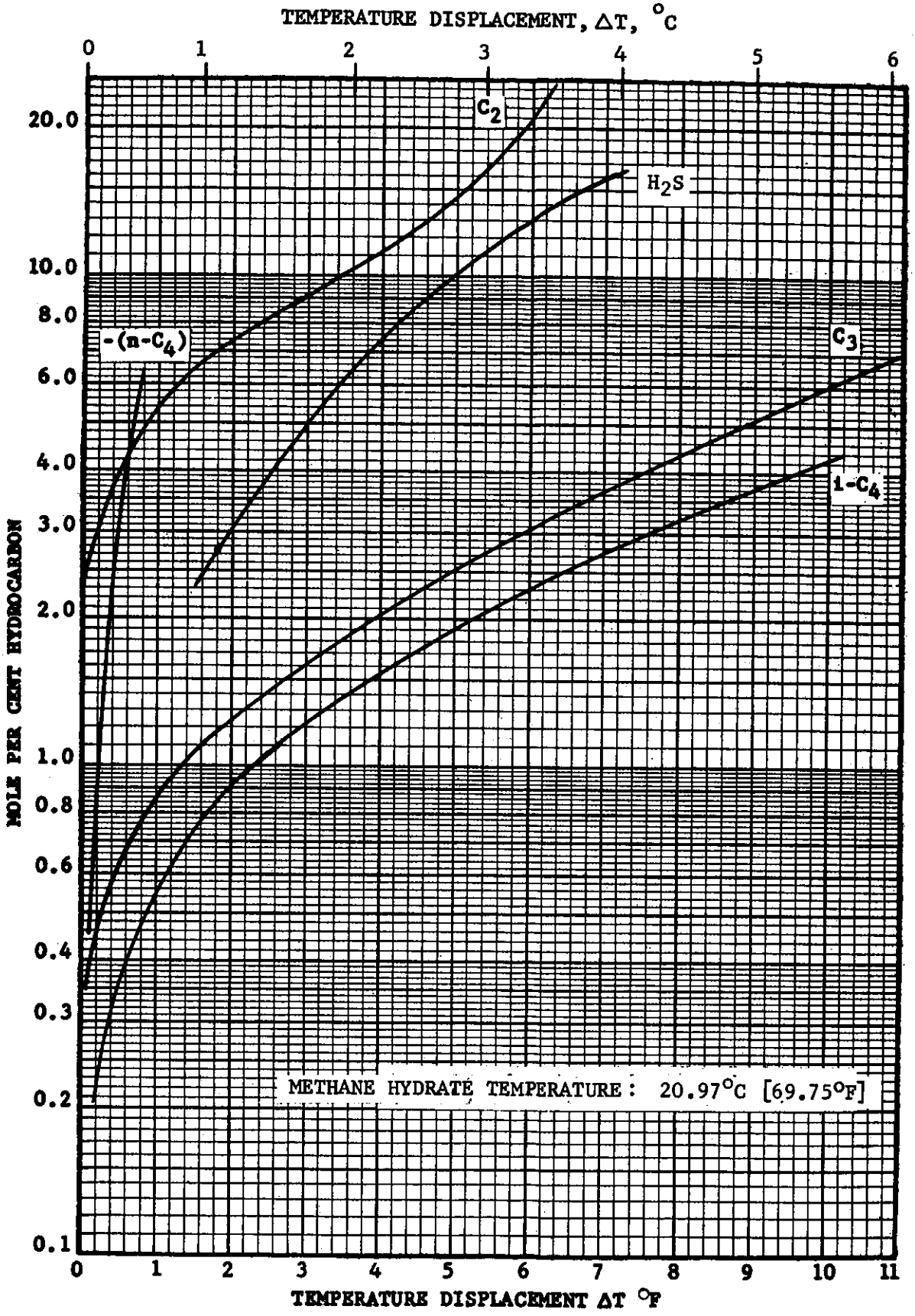


Figure 6.20(a) Hydrate Prediction Correlations at 27.6 MPa

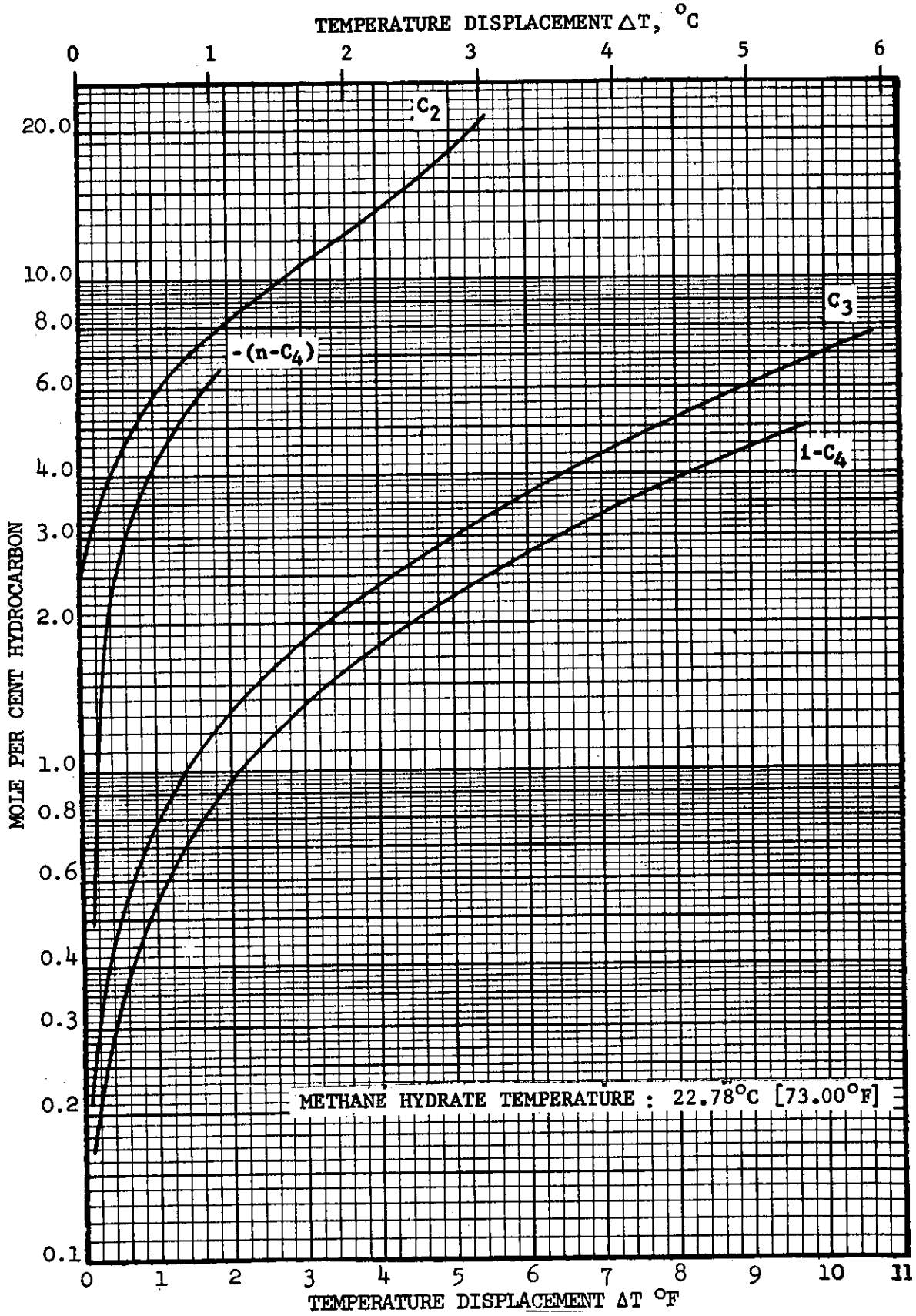


**Figure 6.21 Hydrate Prediction Correlations at 34.5 MPa**

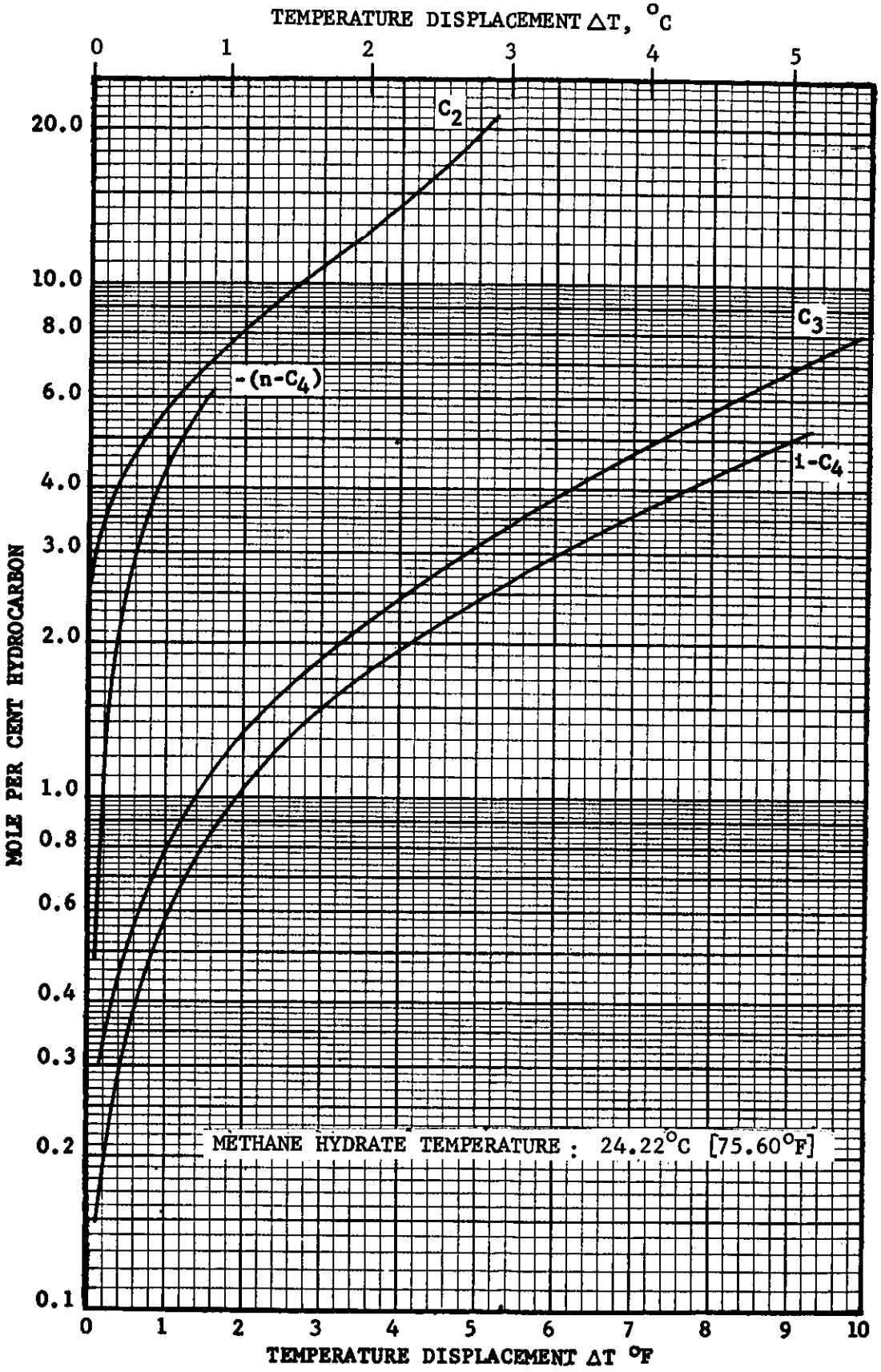


Figure 6.21(a) Hydrate Prediction Correlations at 41.4 MPa

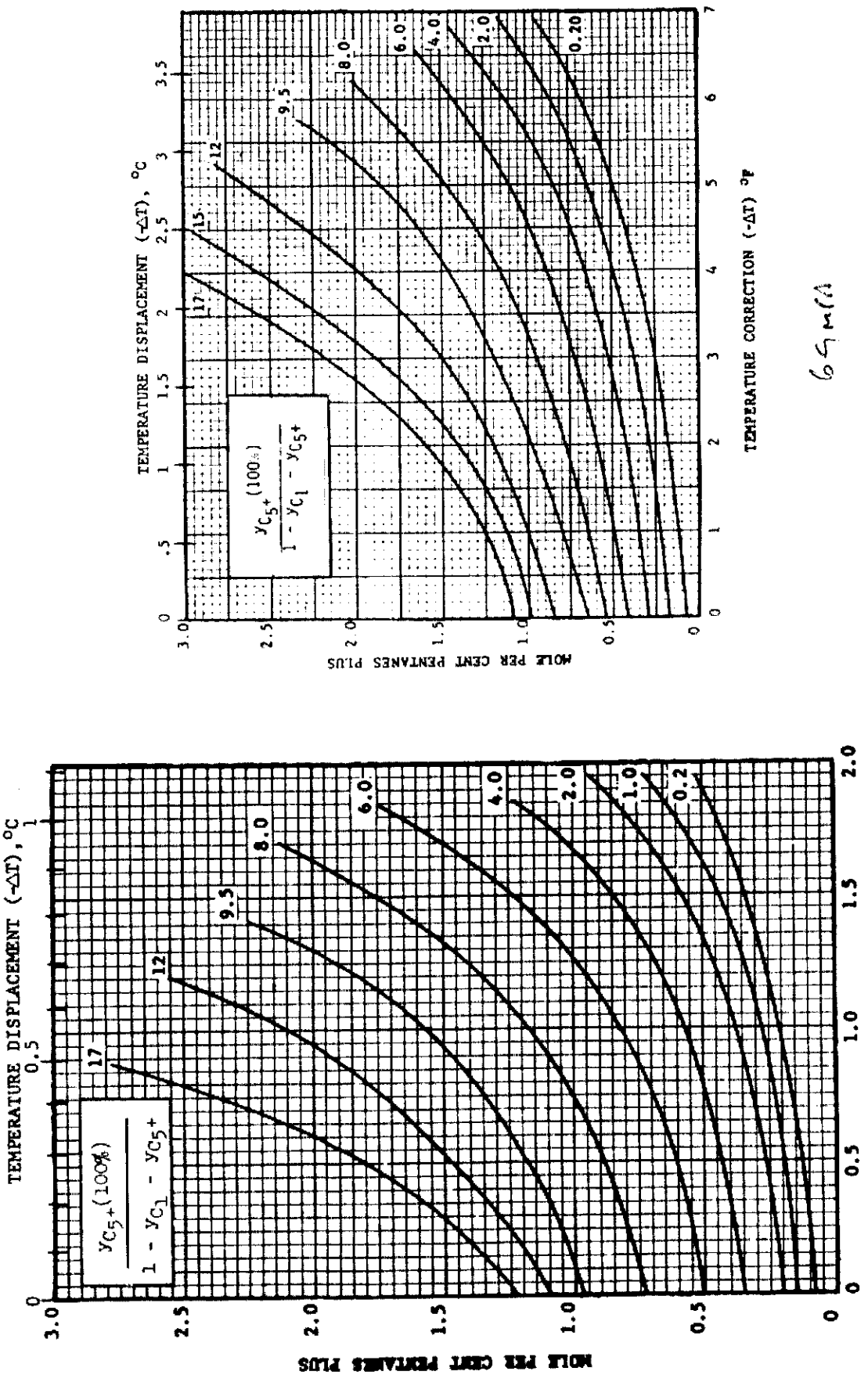


Figure 6.22 Hydrate Prediction Correlations for Non-Hydrate Formers

## McLeod-Campbell Method

This work[6.22] is for use with high pressure gases above about 35-40 MPa [5000-6000 psia].[6.21] Early work indicated erroneously that gas hydrate forming curves approach the pure methane curve at these high pressures. This work proves that said curves are parallel to the methane curve and have essentially the same slope for all gas mixtures.

A specific correlation was prepared from 41.4-69 MPa [6000-10 000 psia] using a modified Clapeyron equation to describe the energy of phase transformation. Using available data this was reduced to the simple equation

$$T = A\,(C')^{0.5} \qquad (6.6)$$

Where:

| | | Metric | English |
|---|---|---|---|
| T | = hydrate forming temperature | K | °R |
| A | = correlation factor | 2.16 | 3.89 |
| C′ | = component factors from the following table | | |

| Pressure | | C Values | | | | |
|---|---|---|---|---|---|---|
| MPa | psia | $C_1$ | $C_2$ | $C_3$ | $iC_4$ | $nC_4$ |
| 41.4 | 6000 | 18 933 | 20 806 | 28 382 | 30 696 | 17 340 |
| 48.3 | 7000 | 19 096 | 20 848 | 28 709 | 30 913 | 17 358 |
| 55.2 | 8000 | 19 246 | 20 932 | 28 764 | 39 935 | 17 491 |
| 62.1 | 9000 | 19 367 | 21 094 | 29 182 | 31 109 | 17 868 |
| 69.0 | 10 000 | 19 489 | 21 105 | 29 200 | 30 935 | 17 868 |

In using Equation 6.6 one expresses the gas composition in terms only of the relative quantity of methane through n-butane. All heavier molecules are ignored. Multiply this pseudo mol fraction by each component's "C" value from the table to find a composite value for substitution into Equation 6.6.

**Example 6.5:** Calculate the hydrate forming temperature of a gas at 41.4 MPa [6000 psia] with the pseudo analyses shown.

| Component | Mol Fr. | C | C′ |
|---|---|---|---|
| $C_1$ | 0.906 | 18 933 | 17 153 |
| $C_2$ | 0.066 | 20 806 | 1373 |
| $C_3$ | 0.018 | 28 382 | 511 |
| $iC_4$ | 0.005 | 30 696 | 153 |
| $nC_4$ | 0.005 | 17 340 | 87 |
| Total | 1.000 | | 19 277 |

From Eqn. 6.6, $T = (2.16)(19\,277)^{0.5} = 300$ K = 27°C  $T = (3.89)(19\,277)^{0.5} = 540$°R = 80°F

Reference 6.23 presents hydrate data for a lean natural gas at pressures to 100MPa [14 500 psia].