Freezing Points of Binary Mixtures of Methane

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The experimental freezing-point data of the methane-*n*-hexane and the methane-*n*-octane binaries are presented and compared with the methane-carbon dioxide system investigated by Donnelly and Katz. A step-by-step variation of the freezing point in the paraffin homologous series is exploited to provide reasonably accurate extrapolation of the experimental data on the two binaries and scattered freezing-point data on the methane-*n*-butane mixture to other paraffin hydrocarbon mixtures of methane in which the heavier constituent ranges from ethane to *n*-nonane, inclusive.

A composite graph of the freezing points of the various binaries with methane, from ethane to *n*-nonane, is presented.

Recently the purification of natural gas as well as other petroleum hydrocarbons by low-temperature separation processes has received increasing attention, owing to the technical and economic attractiveness of the possibilities of effecting such a separation by physical rather than chemical means. An example of such an application has been the removal of ethane and ethylene from natural and refinery gases by low-temperature distillation.

To exploit the possibilities of such processes for the petrochemical industries, basic information must first be obtained in the form of low-temperature phase and volumetric properties of the hydrocarbon mixtures involved. With such fundamental information, processes may be designed to evaluate the feasibility of these proposed low-temperature processes as compared with existing procedures for effecting purification. Were it not for the lack of basic knowledge in this field, applications of the low-temperature-process technique would no doubt be more widespread than they are today.

Sage (*1*) has summarized the present knowledge of the physical properties of binary systems of the paraffin hydrocarbons from methane through decane. Deschner, *et al.* (*2*), and Mullins, *et al.* (*3*), have proposed that nitrogen be separated from natural gas by distillation at low temperatures. P. C. Davis, *et al.* (*4*), have contributed data on the phase and volumetric studies of natural gas. Aroyan and Katz (*5*) have investigated the low-temperature equilibria in the hydrogen-*n*-butane binary, and Brown and Stutzman (*6, 7*) reported on the low-temperature equilibrium constants for the nitrogen-methane-ethane system.

This paper presents the experimental data of Beck (*8*) on the freezing points of the methane-*n*-hexane binary and those of Papahronis (*9*) on the freezing points of the methane-*n*-octane system. In addition, these data are compared with those of Donnelly and Katz (*10*) on the methane-carbon dioxide binary, together with extrapolated values of those other paraffin hydrocarbon mixtures of methane in which the heavier constituent ranges from ethane to nonane, inclusive.

The work of Beck (*8*) and Papahronis (*9*) was carried out in the apparatus previously described by Kohn and Kurata (*11*).

DATA USED

The experimental freezing-point determinations of the methane-*n*-hexane binary as measured by Beck (*8*) are presented in Table 1.

TABLE 1. FREEZING POINT OF CH_4-nC_6H_{14} MIXTURES

Mole fraction nC_6H_{14}	Freezing point, °F.
1.00	−138.0
0.90	−141.6
0.80	−145.0
0.70	−149.2
0.60	−153.0
0.50	−157.6
0.40	−161.8
0.30	−169.0
0.20	−181.8
0.10	−207.4
0.05	−236.0
0.0	−296.0

The freezing-point data of Papahronis (*9*) on the methane-*n*-octane system are given in Table 2

TABLE 2. FREEZING POINT OF CH_4-nC_8H_{18} MIXTURES

Mole fraction nC_8H_{18}	Freezing point, °F.
1.00	− 70.3
0.92	− 71.9
0.895	− 73.0
0.835	− 74.5
0.762	− 77.2
0.643	− 81.5
0.56	− 84.0
0.0	−296.0

A summary of the freezing point data of Donnelly and Katz (*10*) concerning the methane-carbon dioxide binary is presented in Table 3.

TABLE 3. FREEZING POINT OF CH_4-CO_2 MIXTURES

Mole fraction CO_2	Freezing point, °F.
1.00	− 72
0.90	− 74
0.80	− 77
0.70	− 81
0.60	− 83.5
0.543	− 86
0.50	− 86.5
0.18	−117
0.0	−296

TABLE 4. FREEZING POINTS OF PARAFFIN HYDROCARBONS

Compound	Freezing point, °F.	Difference in freezing point, °F.
C_2H_6	−298	
C_3H_8	−306	8
nC_4H_{10}	−217	
nC_5H_{12}	−201.5	−15.5
nC_6H_{14}	−138	
nC_7H_{16}	−131.5	− 6.5
nC_8H_{18}	− 70.3	
nC_9H_{20}	− 64	− 6.3

TABLE 5. FREEZING POINTS OF PARAFFIN HYDROCARBONS

Compound	Freezing point, °F.	Difference in freezing point, °F.
C_3H_8	−306	
nC_4H_{10}	−217	−89
nC_5H_{12}	−201.5	
nC_6H_{14}	−138	−63.5
nC_7H_{16}	−131.5	
nC_8H_{18}	− 72	−59.5

EXTRAPOLATED FREEZING POINTS OF OTHER METHANE MIXTURES

When the freezing points of the pure paraffin hydrocarbons are tabulated and paired as in Tables 4 and 5, some interesting observations may be made.

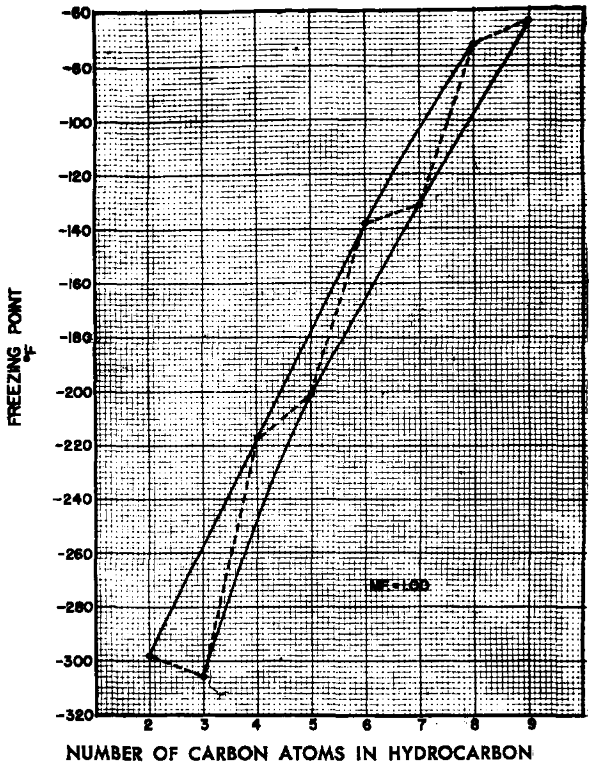

Fig. 1. Step-by-step variation in freezing points of hydrocarbons.

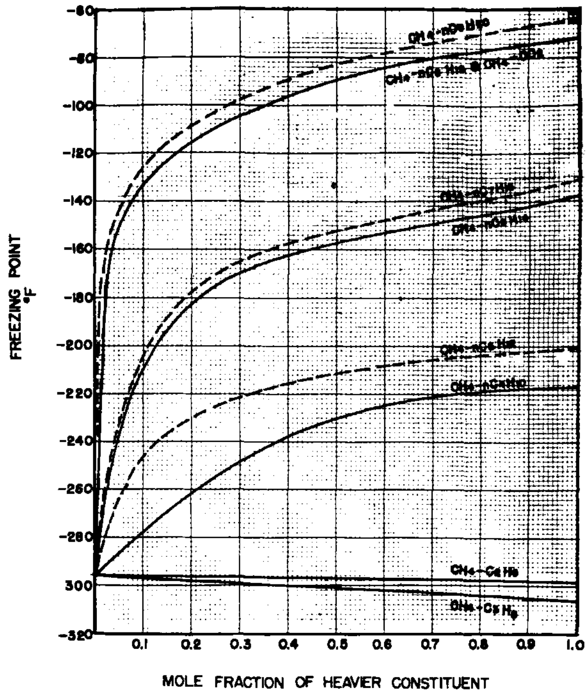

Fig. 2. Freezing point of methane mixtures.

It is evident from Table 4 that the freezing point increases as the paraffin series advances, with the sole exception of that for C_3H_8. Furthermore the freezing points of the hydrocarbons do not increase smoothly as the series progresses but appear to increase by steps. This is illustrated analytically in the comparison of Tables 4 and 5. In Table 4 the hydrocarbons are paired beginning with C_2H_6, and in Table 5 the paired hydrocarbons start with C_3H_8. The differences in the freezing points of the various pairs of hydrocarbons are shown in the last entries of the two tables.

When the hydrocarbons are paired, as in Table 4, the average difference in the freezing points of the pairs is about 10°F. On the other hand, when the compounds are paired, as in Table 5, the average difference in the freezing points is seen to be much higher, about 70°F. This characteristic is shown graphically in Figure 1, in which the freezing points of the paraffins are plotted against the number of carbon atoms in the hydrocarbon. In this graph the dotted curve connects successive members of the paraffin series from ethane to *n*-nonane, inclusive, and illustrates the step-by-step nature of the variation in the freezing points. However when the series is divided into two groups containing those members having an even number and those having an odd number of carbon atoms, each of these groups separately shows a smooth change in the freezing point. The two solid curves in Figure 1 illustrate this.

These observations indicate that the freezing point of a given paraffin hydrocarbon depends a great deal upon whether the number of carbon atoms in that hydrocarbon is odd or even.

Since an arrangement of the pairs of hydrocarbons like that of Table 4 gives a low value for the difference in freezing points for the pairs, it suggests that reasonably accurate values for the freezing points of methane–*n*-nonane mixtures, for example, can be had by simple extrapolation of the methane–*n*-octane data. Likewise the freezing points of the methane–*n*-heptane mixtures can be had by extrapolation of the methane–*n*-hexane data.

Since the freezing points of ethane and propane are nearly the same as the freezing point of methane, it is believed that a plot of the freezing point of their methane mixtures as a function of concentration can be taken as a simple, straight line with reasonable accuracy. With this information and additional scattered data of the freezing points of the methane–*n*-butane binary, the freezing-point curve of the methane–*n*-pentane binary was found from a series of cross plots of the foregoing data at various mole fractions.

An item of note is that the freezing-point curves of the binaries methane–*n*-octane and methane–carbon dioxide are reasonably coincident over that portion of the experimental data presented in Tables 2 and 3.

The final results are given in Figure 2, a composite graph of the freezing points of the various binary mixtures with methane from ethane to *n*-nonane, inclusive. In this graph the solid curves were plotted from experimental data and the dotted curves were obtained by extrapolation, as described above.

Figure 2 should be of value in approximating the freezing points of the various binary mixtures of methane and other paraffins and in approximating the maximum concentrations of the higher hydrocarbon which can be tolerated in methane before the solids begin to form.

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