4. The methyl radicals subsequently combine with azomethane molecules yielding more complicated radicals and molecules.

5. The ethane and other alkane gas produced during the photolysis of azomethane results from a decomposition reaction involving the more complicated radicals and molecules. Practically none of the ethane formed results from a combination of the methyl radicals; methyl radicals do not combine readily at ordinary temperatures to form ethane.

6. Some compound formed by the interaction of nitric oxide and the products of the photolysis of azomethane is thermally unstable, yielding mainly substances which are soluble in acid solution.

7. Some compound so formed is more stable to light than is azomethane. When it is decomposed by light, nitrogen and a small amount of alkane gas are among the products.

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[CONTRIBUTION OF THE RESEARCH LABORATORY OF THE BATAAFSCHE PETROLEUM MAATSCHAPPIJ]

Freezing Points of a Number of Pure Hydrocarbons of the Gasoline Boiling Range and of Some of their Binary Mixtures

BY J. SMITTENBERG, H. HOOG AND R. A. HENKES

The freezing point or melting point is one of the most useful physical properties in the identification of chemical substances and in the verification of their degree of purity.

For this reason we started an investigation of the freezing points of a number of hydrocarbons of the gasoline boiling range, which were available in our laboratory. Since it was desirable to have some idea of the effect of impurities upon the behavior of the hydrocarbons when freezing, a number of binary hydrocarbon mixtures were also tentatively examined.

1. Preparation and Purification of the Hydrocarbons.—Nearly all the hydrocarbons were prepared synthetically, some in our laboratory and some in the laboratory for organic chemistry of the University of Amsterdam under the guidance of Professor Dr. J. P. Wibaut.

As a rule the hydrocarbons were purified by sharp rectification with a fractionating column of about 22 theoretical plates. Each preparation was separated into at least ten fractions and only those fractions whose boiling points differed by less than 0.2° and whose refractive indices differed by less than 0.0002 were accepted as "pure."

The preparation and examination of these hydrocarbons will be described shortly *in extenso* in a separate article. The provisional results of the determinations of the boiling point, the refractive index and the freezing point and/or melting point are given in Table I. A number of other physical properties are at present being determined.

2. Apparatus and Methods for the Determination of Freezing and Melting Points.—A platinum resistance thermometer, consisting of about 85 cm. of platinum wire 0.033 mm. in diameter and made to De Leeuw's pattern,[1] was used for most of the determinations. The total length of this thermometer, S, was 20 cm., its diameter 0.8 cm., and the volume of the actual measuring part, 1.5 cc.

In some instances a larger thermometer, L, was used, consisting of 100 cm. of platinum wire 0.05 mm. in diameter. The total length of this thermometer was 50 cm., its diameter 1.2 cm. and the volume of the measuring part 5 cc.

A Wheatstone bridge was used to measure the resistance; the values of the deflections of the galvanometer were calibrated with the aid of standard resistances, which could be placed in the bridge instead of the thermometer.

Four or five fixed points were used for the temperature standardization of the resistance thermometers, as follows

Fixed point no.	Substance	Accepted temp., °C.		Resistance of thermometer in ohms	
				S	L
1	Ice	M. p.	0.00	99.06	45.38
2	Mercury	F. p.	− 38.87	84.85	38.45
3	*n*-Heptane	F. p.	− 90.8	65.65	29.08
4	*n*-Pentane	F. p.	−129.73	50.82	21.87
5	Oxygen	B. p.	−183.0	30.7	

The *n*-heptane was a commercial product, obtained from the California Chem. Co., the freezing point of which is guaranteed by the National Bureau of Standards to be −90.8°. The *n*-pentane was a synthetic product which, according to its physical constants and cooling curve, was very pure. The value given by Mair[2] was accepted for its freezing point.

The following procedure was adopted for rapid conversion of intermediate resistances to the corresponding temperatures.

For each thermometer the constants a and b of the formula

$$t = aR - b \qquad (1)$$

were calculated from the fixed points 2 and 3. In this formula t represents the fixed temperature in degrees centi-

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[1] De Leeuw, *Z. physik. Chem.*, **77**, 304 (1911).

[2] B. J. Mair, *Bur. Standards J. Research*, **9**, 457 (1932).

TABLE I

CRYSTALLIZATION DATA OF PURE HYDROCARBONS

The data, quoted from literature, are taken from Parks and Huffman,[3] unless otherwise stated. For sources, see below.

	Literature data				Observation of the authors of this paper					
Hydrocarbon	M. p. or f. p., °C.	Transition point, °C.	Heat of fusion, cal./mole	Heat of transition, cal./mole	B. p. (760 mm.), °C.	Refractive index, $n^{20}D$	F. p., °C.	M. p., °C.	Transition point, °C.
Paraffins									
n-Pentane	−129.7[2]	.....	2000	..	36.0	1.3580	−129.7	.....	...
2-Methylbutane	−160.5	.....	1220	..	27.8	1.3552	−160.6	.....	...
n-Hexane	− 95.0	.....	3110	..	68.8	1.3751	− 95.5	.....	...
2-Methylpentane	−143 ?[4]	.....	..	..	60.3	1.3716	Glass	.....	...
3-Methylpentane	−118 ?[4]	.....	..	..	63.3	1.3769	Glass	.....	...
2,2-Dimethylbutane	− 98.2[5]	.....		..	49.7	1.3691	−100.5	.....	abt. −146
2,3-Dimethylbutane	−127.8[6] or −135.1[5]	.....	..	..	58.1	1.3752	−128.5	−128.2 and −136.8 (metastable)	abt. −142
n-Heptane	− 90.6	.....	3370	..	98.4	1.3878	− 90.8	.....	...
2-Methylhexane	−119.1	.....	2120	..	90.1	1.3852	−118.5	−118.2	...
2,2-Dimethylpentane	−125.0	.....	1400	..	79.3	1.3822	−124.0	.....	...
2,3-Dimethylpentane (*as*)	Glass[7]	.....	..	..	89.8	1.3921	Glass	.....	...
2,4-Dimethylpentane	−120.6	.....	1600	..	80.6	1.3820	−119.1	.....	...
3,3-Dimethylpentane	−134.9	.....	1690	..	86.1	1.3911	−135.7	−135.0	...
2,2,3-Trimethylbutane	− 25.4	−152.1	530	570	81.0	1.3899	− 26.3	.....	abt. −156
n-Octane	− 57.3	.....	4930	..	125.8	1.3979	− 56.8	− 56.8	...
3-Methylheptane (*as*)	.....	.....	..	..	119.1	1.3988	Glass	.....	...
2,3-Dimethylhexane (*as*)	.....	.....	..	..	115.8	1.4015	Glass	.....	...
2,5-Dimethylhexane	− 90.7[8]	.....	..	..	109.3	1.3930	− 94.0	.....	...
3,4-Dimethylhexane (*as*)	.....	.....	..	..	117.9	1.4044	Glass	.....	...
2,2,3-Trimethylpentane (*as*)	.....	.....	..	..	110.1	1.4032	Glass	.....	...
2,2,4-Trimethylpentane	−107.8	.....	2160	..	99.1	1.3917	−107.6	.....	...
3-Methyl-3-ethylpentane	.....	.....	..	..	118.4	1.4081	− 91.1	− 90.9	...
2,2,3,3-Tetramethylbutane	+104	−125.0	1700	480	...	....	+101.5	+101.2	−119.2
n-Nonane	− 53.9	− 51.5?	*hf* + *ht* = 5280		150.7	1.4060	− 53.8	− 53.7	.....
Naphthenes									
Ethylcyclobutane	.....	.....	..	..	70.7	1.4023	−143.2	.....	.....
Cyclopentane	− 94.8[9]	.....	..	..	49.2	1.4065	− 94.3	.....	−151.5
Methylcyclopentane	−143.0	.....	1640	..	71.9	1.4100	−142.7	−142.4	.....
Cyclohexane	+ 6.2	− 87.2	620	1610	80.8	1.4262	+ 6.4	.....	− 87.0
Methylcyclohexane	−126.9	.....	1590	..	100.8	1.4231	−126.4	−126.3	.....
Isopropylcyclohexane	− 90.6[10]	.....	..	..	154.5	1.4410	− 89.8	− 89.8	.....
Aromatics									
Benzene	+ 5.5	.....	2350	..	80.1	1.5011	+ 5.5	.....	.....
Toluene	− 95.1	.....	1580	..	110.8	1.4962	− 95.6	.....	.....
Isopropylbenzene	− 96.9[10]	.....	..	..	152.4	1.4912	− 96.2	− 96.1	.....

grade and R the corresponding resistance of the thermometer in ohms. The deviations of the fixed points 1, 4 and 5 from this formula were plotted as a function of the temperature and interconnected by means of a smooth curve. The intermediate resistances were converted to degrees centigrade by means of formula (1) and then corrected by means of the above-mentioned curve.

During the freezing point tests the hydrocarbon was in a glass tube enclosed in a vacuum jacket. This jacket was placed in a bath of carbon dioxide–alcohol or liquid nitrogen. The rate of cooling was regulated by varying the pressure in the vacuum jacket. The same equipment, now placed in an empty Dewar vessel or in an alcohol-bath the temperature of which was regulated by the addition of solid carbon dioxide, was used for the melting point test (from heating curves).

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(3) G. S. Parks and H. M. Huffman, *Ind. Eng. Chem.*, **23**, 1138 (1931).

(4) J. H. Bruun and M. M. Hicks-Bruun, *ibid.*, **5**, 933 (1930).

(5) H. v. Risseghem, *Bull. soc. chim. belg.*, **30**, 8 (1921); **31**, 62 (1922).

(6) G. B. Kistiakowsky, THIS JOURNAL, **58**, 137 (1936).

(7) G. Edgar, G. Calingaert and R. E. Marker, *ibid.*, **51**, 1483 (1929).

(8) J. Timmermans and Mme. Hennaut-Roland, *J. chim. phys.*, **29**, 529 (1932).

(9) G. Chavanne, *Bull. soc. chim. belg.*, **31**, 338 (1922).

(10) J. Timmermans, *ibid.*, **36**, 502 (1927).

This method did not produce very satisfactory results in the freezing point tests of a number of hydrocarbons having freezing points between approximately −70 and −110°, because the difference between the freezing point temperature of the hydrocarbon and the bath temperature (−196°) was too great. Matters were greatly improved by placing an electric heating coil within the evacuated part of the vacuum jacket.

During the determination of the heating and cooling curves the material under test was stirred by means of the resistance thermometer, at least if not impeded by too large a quantity of solid substance.

3. Freezing Point Determinations of Pure Hydrocarbons.—The results of the present investigation are collected in Table I and a few characteristic examples of cooling and heating curves are shown in Figs. 1, 2 and 3.

The **normal paraffin hydrocarbons** C_5 to C_9 inclusive are found to crystallize easily and show no, or only slight, undercooling. No transition temperatures were observed. We were not able to confirm Parks and Huffman's observation[3] of a transition point of *n*-nonane slightly below its freezing point.

Several **iso-paraffins**, chiefly those with a strongly branched, but symmetrical, structure also crystallize readily, *e. g.*, 2,2,3-trimethylbutane, 2,2,4-trimethylpentane, 2,2,3,3-tetramethylbutane, 3-methyl-3-ethylpentane (see Fig. 1).

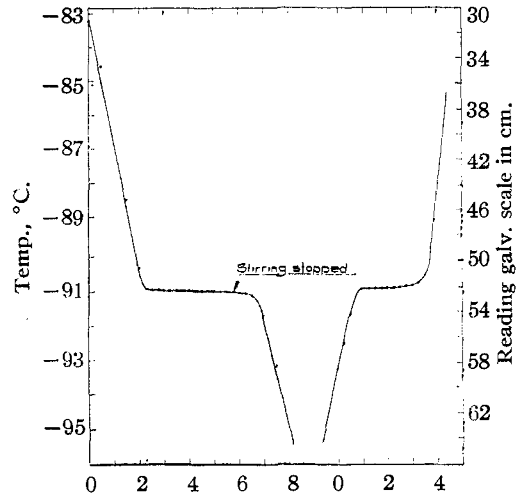

Fig. 1.—Cooling and heating curves of 3-methyl-3-ethylpentane: 5-cc. sample.

There are many other iso-paraffins, on the other hand, which produce undercooling in varying degrees, *e. g.*, 2-methylhexane, 2,2-dimethylpentane, 2,4-dimethylpentane, 2,5-dimethylhexane. Some iso-paraffins, mainly those which possess an asymmetrical carbon atom, could not be brought to crystallization at all and set to a glass, *e. g.*, 2,3-dimethylpentane, 2,2,3-trimethylpentane, 3,4-dimethylhexane, but also 2-methylpentane and 3-methylpentane.[11]

The following few iso-paraffins, however, solidified practically without any undercooling, but did not give a horizontal freezing plateau: 2,2-dimethylbutane (see Fig. 2), 2,3-dimethylbutane (Fig. 3), 2,2,3-trimethylbutane, 2,2,3,3-tetramethylbutane. As these hydrocarbons fully meet the demands of purity mentioned in paragraph 1, it must be assumed that the heat of crystallization is inadequate in this case to maintain the substance at the freezing point during the process of solidification in the given cooling conditions.

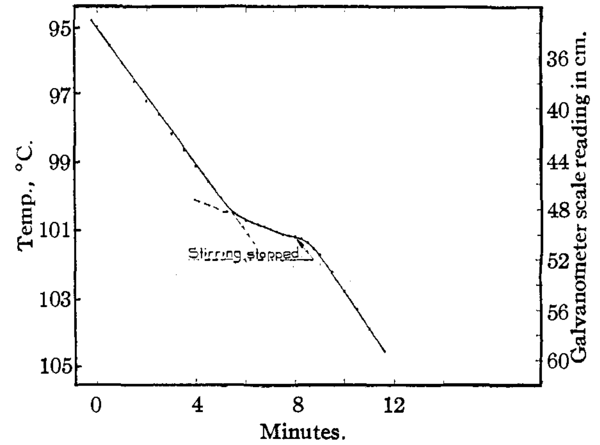

Fig. 2.—Cooling curve of 2,2-dimethylbutane: 5-cc. sample.

Very remarkably, in all these cases we were able to show the existence of a transition temperature, more or less far below the freezing temperature. 2,3-Dimethylbutane was the most beautiful example of these cases of enantiotropy; see Fig. 3.

Ethylcyclobutane deserves special attention among the **naphthenes** examined, because the literature so far has provided no reliable data on this hydrocarbon. After very careful purification a number of fractions were obtained of practically identical freezing point. The substance has a strong tendency toward undercooling and glass formation. By slow cooling or by seeding very reliable freezing plateaus can nevertheless be obtained.

The other naphthenes and **aromatics** examined, with the exception of those easily crystallizing substances, cyclohexane and benzene, produced a pronounced degree of undercooling, yet showed quite satisfactory freezing plateaus after crystallization had begun. Both cyclopentane and cyclohexane possess a transition temperature.

4. Freezing Point Diagrams of Some Binary Hydrocarbon Mixtures.—A review of the literature data on freezing point diagrams of binary mixtures of hydrocarbons within the gasoline boiling range discloses the fact that nearly all the systems examined[12] show a eutectic point,

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[11] Bruun and Hicks-Bruun[4] report −143° as the freezing point of 2-methylpentane and −118° for 3-methylpentane on the strength of an exceedingly subtle discontinuity in the cooling curve. We were unable to duplicate these observations. We could confirm, however, the eutectic temperature (−153°) observed by them for a mixture of 2-methylpentane and carbon dioxide. In a paper, presented before the Petroleum Division of the Rochester Meeting of the American Chemical Society (Sept., 1937), Bruun, Hicks-Bruun and Faulconer described a new method for determining the freezing point of 2-methylpentane. The result was a flat plateau in the cooling curve at −154.0°. Attempts to determine the freezing point of 3-methylpentane in the same way failed, however.

[12] S. Sapgir, *Bull. soc. chim. belg.*, **38**, 392 (1929); J. Timmermans, *ibid.*, **43**, 626 (1934); **37**, 409 (1928); J. H. Bruun and M. M. Hicks-Bruun, *Bur. Standards J. Research*, **8**, 525 (1932); Paterno

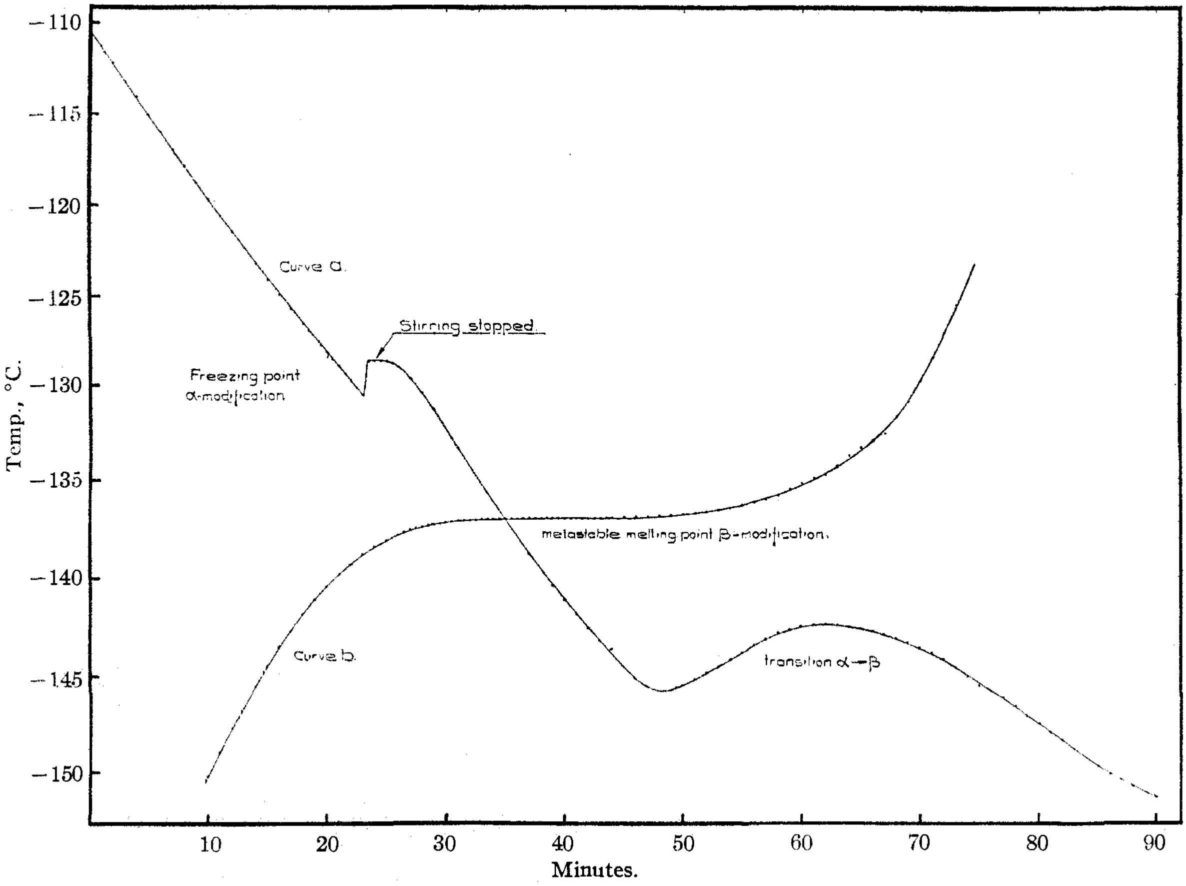

Fig. 3.—Cooling and heating curves of 2,3-dimethylbutane: 35-cc. sample.

while the freezing point curves of the components as a rule more or less conform to the equation for the "ideal freezing point curve": $\log x = A/T + B$ where x represents the mole fraction of the component concerned and T the initial freezing point of the mixture expressed in degrees absolute.

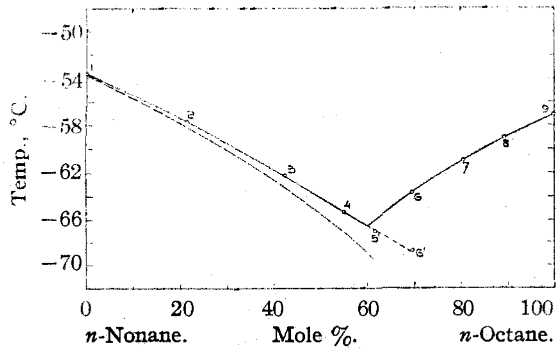

Fig. 4.—System *n*-octane–*n*-nonane: — observed; - - - calcd. (Q = 5280 cal./mole).

There are, however, no particulars of binary mixtures of normal paraffins, nor of binary mixtures of iso-paraffins. We therefore examined some of these systems in order to find out whether the above generalization may be applied to them too.

Remarkable results were obtained upon the examination of the system *n-octane–n-nonane;* see Fig. 4.

Points 1 to 4 inclusive were determined quite distinctly from clear breaks in the cooling curves. With points 2, 3 and 4 the entire process of crystallization took place within 2–3°. After the considerable delay in the temperature drop within this range a rapid temperature drop followed, without any indication of a eutectic temperature.

Upon heating the frozen mixtures 1 to 4, inclusive, we were also able to determine final melting points, both visually and on the basis of a break in the heating curve. These final melting points tallied perfectly well with the initial freezing points derived from the cooling curves.

On cooling mixtures 5 and 6 behaved exactly similarly to 2, 3 and 4: solidification set in without any undercooling at points 5′ and 6′. Upon heating the frozen mixtures, the final melting point of mixture 5 was also at 5′; that of mixture 6 was however not at 6′, but at the far higher temperature 6.

The initial freezing point of mixtures 7 and 8 could not be determined, owing to rather marked undercooling; the indicated points 7 and 8 were determined only from heating curves.

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and co-workers, *Gazz. chim. ital.*, **24**, 208 (1894); **27**, 481 (1897); A. Nakatsuchi, *Sci. Rep. Tôhoku Imp. Univ.*, **15**, 53 (1926); A. Nakatsuchi, *J. Soc. Chim. Ind. Japan*, **32**, 333 (1929); Mascarelli and Pestalozza, *Gazz. chim. ital.*, **38**, 38 (1809); Robert, *Bull. soc. chim.*, **25**, 463 (1919); Sh. Mitsukuri and A. Nakatsuchi, *Sci. Rep. Tôhoku Imp. Univ.*, **15**, 45 (1926); I. Seto, *C. A.*, **22**, 4127 (1928); J. H. Bruun and M. M. Hicks-Bruun, *Bur. Standards J. Research*, **7**, 799 (1931).

Finally *n*-octane (point 9) again showed a distinct freezing point without any undercooling and upon heating a melting point coinciding exactly with the freezing point.

Plotted in a $\{\log (1 - x), 10^4/T\}$-diagram, points 2, 3, 4, 5′ and 6′ show a gradually increasing departure from the theoretical straight line for $Q = 5280$ cal. (molecular heat of fusion of *n*-nonane according to Parks and Huffman[13]). The points 9, 8, 7 and 6 practically coincide in the $\{\log x, 10^4/T\}$-diagram with the theoretical line for $Q = 4930$ cal. (*n*-octane), point 5′ is distinctly outside this and obviously belongs to the *n*-nonane branch.

From the foregoing we think we may conclude that *n*-nonane and *n*-octane form an interrupted series of mixed crystals. The crystals rich in *n*-nonane are formed easily and differ but little in composition from the liquid with which they are in equilibrium. The crystals rich in *n*-octane, however, are formed with far greater difficulty (undercooling) and have a far larger *n*-octane content than the liquid with which they are in equilibrium. Apparently therefore *n*-octane is readily absorbed in the crystal lattice of *n*-nonane, whereas *n*-nonane is with difficulty taken up in the lattice of *n*-octane. As these mixed crystals rich in *n*-octane do not separate out of the liquid easily the eutectic point at −66.5° does not appear as a plateau in the cooling curves.

Unlike the *n*-octane–*n*-nonane system, in which mixed crystal formation occurs, all the binary mixtures of normal paraffins and iso-paraffins examined show ideal freezing point curves. In addition to the data, known from literature, we examined the systems: *n*-heptane–2,2,4-trimethylpentane (eutectic pt.: −114.4°; 24 mol. % *n*-heptane); *n*-octane–2,2,4-trimethylpentane (eutectic pt.: −108.5°; 3 mol. % *n*-octane); and *n*-hexane–2,3-dimethylbutane (eutectic pt.: −138°; 7 mol. % *n*-hexane).

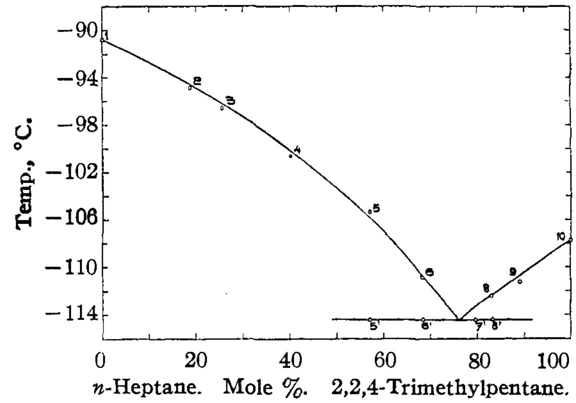

Fig. 5.—System *n*-heptane–2,2,4-trimethylpentane.

In the case of the first system (see Fig. 5) both the *n*-heptane and the 2,2,4-trimethylpentane freezing point curves are practically ideal; with the last two systems, the freezing points of the components are so far apart and the eutectic point is consequently so one-sided that only the freezing point curves of the normal paraffins were determined; these prove to concord very well with the formula for the ideal freezing point curve from $x = 1$ to $x = 0.3$ to 0.2.

With nearly all the binary mixtures of iso-paraffins we had trouble with glass formation. Only two systems, a component of each of which is the high-melting 2,2,3,3-tetramethylbutane, produced sharply observable initial freezing points. There is, however, a striking difference between the binary system of this component with 2,2,3-trimethylbutane and that with 2,2,4-trimethylpentane. In the latter system the 2,2,3,3-tetramethylbutane freezing point curve corresponds very well with the formula for the ideal freezing point curve; a molecular heat of fusion can be calculated from it amounting to 1810 cal. (Parks and Huffman record 1700 cal.). In the former system, on the other hand, the 2,2,3,3-tetramethylbutane freezing point curve departs considerably from the formula for the ideal freezing point curve. Judging by the results given in Fig. 6, it seems probable that 2,2,3-trimethylbutane and 2,2,3,3-tetramethylbutane constitute an uninterrupted series of mixed crystals.

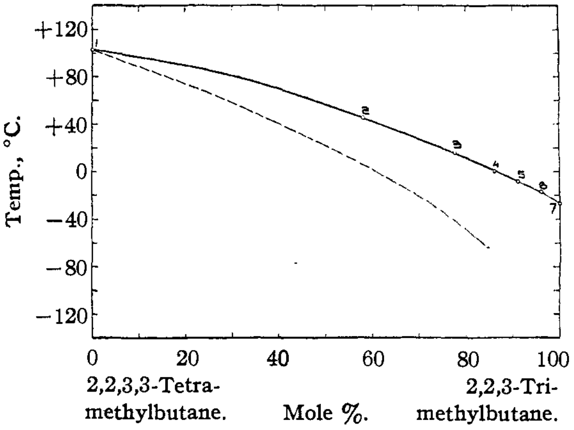

Fig. 6.—System 2,2,3,3-tetramethylbutane–2,2,3-trimethylbutane: — observed; - - - calculated (Q = 1810 cal./mole).

Summary

Freezing point determinations were made of a number of carefully purified hydrocarbons with boiling points within the gasoline boiling range.

All the normal paraffins examined crystallized readily and showed no or only slight undercooling.

Several iso-paraffins, chiefly those with a strongly branched but symmetrical structure, also crystallized easily. Many other iso-paraffins, on the other hand, showed considerable undercooling. Some iso-paraffins, particularly those which possess an asymmetrical carbon atom, could not be brought to crystallization at all and solidified to a glass.

In the case of some other iso-paraffins, which crystallized readily but with a small heat of crystallization, transition points were observed on further cooling.

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(13) According to the data of Parks and Huffman,[8] this value is actually the heat of fusion of the modification, stable at the freezing point, plus the heat of the transition, which takes place at about 2 or 3° below the freezing point. This total heat governs the slope of the nonane-freezing point curve in a binary mixture below the transition temperature of *n*-nonane.

After a varying degree of undercooling, all the naphthenes and aromatics examined could be brought to crystallization; transition points were observed with cyclopentane and cyclohexane.

In addition to published data, we also studied a number of freezing point diagrams of binary hydrocarbon mixtures.

As a rule there is a eutectic point and the freezing point curves of the components conform to the formula for the ideal freezing point curve.

There is probably an interrupted series of mixed crystals in the *n*-octane–*n*-nonane system and a continuous series of mixed crystals in the 2,2,3-trimethylbutane–2,2,3,3-tetramethylbutane system.

Most of the binary iso-paraffin mixtures produced glass formation.

AMSTERDAM, NETHERLANDS RECEIVED AUGUST 10, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, THE HEBREW UNIVERSITY]

The Catalytic Interaction of Ethylene and Heavy Hydrogen on Platinum

BY A. FARKAS AND L. FARKAS

The catalytic interaction of ethylene and hydrogen can involve a number of reactions, such as hydrogenation, exchange of hydrogen atoms,[1] polymerization, and formation of methane and other hydrocarbons.[2] The present paper deals with the first two of these reactions. It contains the study of the exchange reaction and includes some contribution on the mechanism of the hydrogenation obtained by using para-hydrogen and heavy hydrogen as research tools.

The experimental method used was the same as in the previous communications.[3] A platinized platinum foil was used as catalyst. The activity of the catalyst was fairly constant even when the catalyst was heated to elevated temperatures, if care was taken to avoid poisoning by grease or mercury. A freshly prepared catalyst was the most active and its activity decreased somewhat in the course of a few days. In spite of this variation the experiments are comparable since it was always ascertained that the activity should not change when one parameter was being varied during one series of runs. The same numbers of the experiments, *e. g.*, 37a, 37b, etc., will refer to the catalyst being in the same state of activity, which was usually constant during a day.

The reaction vessel had a volume of 60 cc. and was kept in a Dewar vessel at the required temperature by means of an ice- or oil-bath heated electrically. The hydrogenation was followed manometrically and the amount of exchange estimated by determining the change in the D-content of the hydrogen by the micro-thermal conductivity method.[4] This was possible since the D-content of the hydrogen was not changed when left in contact with the catalyst in the absence of ethylene, showing that the catalyst did not absorb or retain any appreciable amount of hydrogen. Since the amount of gas extracted from the reaction vessel was very small, several measurements could be performed in the same run without changing the pressure in the reaction vessel appreciably.

The ethane and ethylene were separated from the hydrogen by passing the gas mixture through a trap cooled with liquid air boiling at 5 to 10 mm. pressure (53°A.).

The progress of the hydrogenation is represented in Fig. 1 at 25° for different hydrogen and ethylene mixtures. It will be recognized that the rate of reaction decreases with increasing ethylene pressure and increases with the hydrogen pressure. The progress of the reaction can be represented approximately by

$$P = P_0 \exp. (-kt) \tag{1}$$

P and P_0 designating the pressure of the reactant not in excess at the time t and $t = 0$, respectively.

The temperature dependence of the hydrogenation is shown in Fig. 2 for mixtures of 40 mm. H_2 + 20 mm. C_2H_4 at 0–78°, log P/P_0 for ethylene being plotted against time. In this region and up to about 150° the temperature dependence of the hydrogenation corresponds to the Arrhenius equation with an energy of activation of 10 kcal. as is shown by curve A in Fig. 3, in

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(1) Farkas, Farkas and Rideal, *Proc. Roy. Soc.* (London), **A146**, 630 (1934).

(2) Morikawa, Trenner and Taylor, THIS JOURNAL, **59**, 1103 (1937).

(3) (a) A. and L. Farkas, *Trans. Faraday Soc.*, **33**, 678 (1937); (b) A. and L. Farkas, *ibid.*, **33**, 827 (1937).

(4) A. and L. Farkas, *Proc. Roy. Soc.* (London), **A144**, 467 (1934).