

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

THE MELTING POINTS OF NORMAL PARAFFINS

BY J. H. HILDEBRAND AND A. WACHTER

RECEIVED MARCH 12, 1929

PUBLISHED AUGUST 7, 1929

In connection with a study of the solubility relations of dicetyl which we are making, it became necessary to have a reliable value for the melting point of the substance. The value given in "International Critical Tables" is 75° , whereas our own material, synthesized according to the method of Sorabji,¹ purified by recrystallization four times from glacial acetic acid and then four times from benzene, gave a melting point of 70.2° . The last crystallization made no change in the melting point. The determinations were made by the aid of a standardized thermometer properly corrected.

A search of the original sources showed the following values, arranged in chronological order: 70 ,¹ 70.0 ,^{2a} $68-70$,³ 69.8 ,^{2b} 71 ,⁴ 70 ,⁵ 70.5 ,^{6a} $74-75$ ⁷ and 70.5 .^{6b}

These values all fall in the neighborhood of 70° , with the exception of the one by Levene, West and van der Scheer. It seemed rather surprising that the expert should have chosen for the tables a single value so divergent from all the others. We accordingly sought a further check, as follows. The normal paraffins might be expected to have melting points increasing regularly with molecular weight, for any differences in crystal form cannot involve much difference in energy with such soft substances as these. We accordingly plotted the melting points of the series from $C_{19}H_{40}$ to $C_{33}H_{78}$ against the number of carbon atoms, as shown in Fig. 1. The points are derived from the references already given. It will be seen that all the points fall rather close to a smooth curve excepting those of Levene, West and van der Scheer, for seven members of the series, these falling from 3 to 5° above the curve. In view of the concordance existing among practically all of the other data, we believe that the figures of these three collaborators should have been rejected instead of selected for "International Critical Tables." Since the curve we have drawn appears to express the other data satisfactorily, except for experimental uncertainties, we suggest the following temperatures read from it as the best values for the melting points of the normal paraffin hydrocarbons from $C_{19}H_{40}$ to $C_{36}H_{74}$.

¹ Sorabji, *J. Chem. Soc.*, **47**, 39 (1885).

² Krafft, (a) *Ber.*, **19**, 2219 (1886); (b) *ibid.*, **40**, 4783 (1907).

³ Mabery, *THIS JOURNAL*, **27**, R35 (1905).

⁴ Meyer and Soyka, *Monatsh.*, **34**, 1163 (1913).

⁵ Späth, *ibid.*, **34**, 1987 (1913).

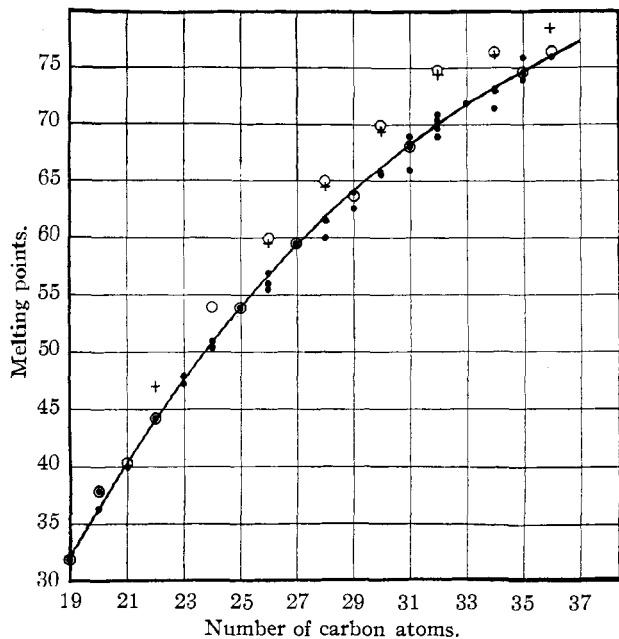
⁶ Gascard, (a) *Compt. rend.*, **159**, 258 (1914); (b) *J. Chem. Soc.*, **106**, 1045 (1914);

(c) *Ann. chim.*, **15**, 332 (1921).

⁷ Levene, West and van der Scheer, *J. Biol. Chem.*, **20**, 521 (1915).

No. of carbon atoms	19	20	21	22	23	24	25	26	27
M. p., °C.	32	36.5	40.5	44	47.5	51	54	57	59.5
No. of carbon atoms	28	29	30	31	32	33	34	35	36
M. p., °C.	62	64	66	68	70	72	73.5	75	76

It will be seen from the figure that there is no real evidence for any alternation between the melting points of the even and odd members



○, "International Critical Tables," ●, various sources; +, Levene, West and van der Scheer.

Fig. 1.

of the series in the range here considered, although it exists for the lower members up to about $C_{15}H_{32}$.⁸

BERKELEY, CALIFORNIA

⁸ Cf. Tsakolotos, *Compt. rend.*, **143**, 1235 (1900).