Hydrocarbon Conversion with Special Reference to the Thermodynamical Calculations for the Isomerization Reactions. I.

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Synopsis. (1) In order to grasp the general trend of isomerization reactions of saturated hydrocarbons, the free energy equations, as a function of temperature convenient for practical calculations, are derived based on one of the more recent data available.

(2) Making use of these derived simple free energy equations, ΔF's at 0°, 25°, 100°, 200° and 300°C. are computed and tabulated and compared with those of other sources.

(3) The free energy equations of some of the useful reactions such as the formation of neohexane by alkylation, and the formation of isooctane by the coupling reaction of isobutene and isobutane are derived and ΔF's are calculated.

(4) Discussions in connection with these thermodynamical calculations for isomerization reactions are presented.

(5) Discussions of the isomerization in connection with so-called "Bond Free Energy Equation" of Bruins and Czarnecki are presented.

(6) In general, isomerization reactions of hydrocarbons, with few exceptions, are favoured thermodynamically at a lower temperature.

(7) Isomerization reactions from simpler structures to more complicated and branched compounds are favoured thermodynamically, more or less, at a lower temperature.

(8) In the isomerization reactions of di- or tri-methylated compounds involving merely an exchange of the position of the carbon to which methyl or ethyl groups are attached, a structure which is more non-symmetrical favours the isomerization thermodynamically at a higher temperature.

(9) Free energy changes involved in the isomerization reactions are of small magnitude as compared with those of ordinary chemical reactions.

(10) The errors involved in the data of the free energy changes of isomerization often amount to a magnitude as big as the free energy change itself. Hence in the selection of data for such calculations, much caution should be taken into consideration.

Introduction. In connection with the investigations of hydrocarbon chemistry, especially in the field of hydrocarbon synthesis, one of the most vital problems is, of course, to obtain justly the desired products without much interference as caused by the various possible side reactions which usually occur almost in any type of synthesis without exception, possibly. However, such a pure reaction is very much desirable and it may be possible in the laboratory scale, but if such a process is industrialized, on account of the necessity of increasing the yield, the pureness of the process is usually sacrificed. Consequently, we are confronted with the situation in which the undesired products must be converted to the desired ones. Such situations are very obviously the case in the liquid fuel synthesis where very many kinds of products are formed, whether desired or not, so that we are naturally forced to separate them and furthermore to proceed with the task of conversion of hydrocarbons, such as normal hydrocarbons changed into the respective isomers.

The isomerization⁽¹⁾ reaction of hydrocarbons, along with cyclization, alkylation, polymerization etc. are very important in improving the quality of liquid fuel. These have long been investigated by various investigators, and their contributions are enormous, above all in the studies on polymer gasoline, the cyclization of heptance to obtain toluene, and the cyclization of octane to xylene, etc., as well as the isomerization of butane, and other normal paraffins, and also the formation of neohexane by alkylation of isobutane in the presence of ethylene, and so on.

The purpose of this paper is to show the thermodynamical possibility of such isomerizations for saturated hydrocarbons (I) and for unsaturates (II)⁽²⁾ in a systematic way. The free energy changes for isomerization reactions⁽¹⁾ often involve errors as many as the free energy change itself. Therefore, in order to get a reasonable estimation of the free energy change by means of the combination of the free energy data from various sources, the data must be very carefully selected. For such precaution, we have consistently based our calculation on one of the most recent investigations⁽³⁾ of which the data seem to have been very consistently selected, although the absolute magnitude may differ from those of other sources. This attitude of calculation is amply justified for this kind of calculation, for the relative magnitude of changes are only important.

Derivations of Free Energy Equations. One of the fundamental equations for the standard free energy of formation as a function of temperature is obviously shown by

$$\Delta F = \Delta H - T\Delta S \tag{1}$$

where ΔF, ΔH, T and ΔS stand for the usual significance—the same notations as used by Lewis and Randall⁽⁴⁾.

As seen in the equation, the free energy of any type of reaction can easily be obtained if the heat of reaction ΔH and the entropy of all substances involved are given at that temperature. The free energy and the heat of formation at any given temperature are connected as:

$$\frac{d(\Delta F/T)}{dT} = -\Delta H/T^2 . \tag{2}$$

From the above-cited relation, the free energy equation may be obtained as a function of temperature, but of course, in order to get the relation usable in practical calculation we must use such a relation as:

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p , \tag{3}$$

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(1) E. Wilson, *Chem. Rev.*, **21** (1937), 129–167; C. D. Nenitzescu, *angew. Chem.*, **52** (1939), 232; H. Shingu, *J. Ind. Chem. Japan*, **46** (1943), 175.

(2) (II) To be published in part II of this series of papers on unsaturated hydrocarbons.

(3) C. M. Thacker, H. O. F. Folkins and E. L. Miller, *Ind. Eng. Chem.*, **33** (1941), 584–590.

(4) Lewis and Randall, "Thermodynamics," 1923.

which is known as Kirchhoff's formula. Using (4) in (3) we obtain (5),

$$\left.\begin{aligned} C_p &= \Gamma_0+\Gamma_1 T+\Gamma_2 T^2+\Gamma_3 T^3+\cdots\cdots\cdots\cdots \\ \Delta C_p &= \Delta\Gamma_0+\Delta\Gamma_1 T+\Delta\Gamma_2 T^2+\cdots\cdots\cdots\cdots\cdots \end{aligned}\right\} \qquad (4)$$

$$\Delta H = \Delta H_0+\Gamma_0 T+1/2\,\Gamma_1 T^2+1/3\,\Gamma_2 T^3+\cdots\cdot \qquad (5)$$

Then substituting it in (2) and by integration of such relation, the desired relation of the free energy as a function of temperature may possibly be obtained, namely:

$$\Delta F^\circ = \Delta H_0-\Gamma_0 T\ln T-1/2\,\Gamma_1 T^2-1/6\,\Gamma_2 T^3+\cdots\cdot+IT\,. \qquad (6)$$

Using these relationships, Thacker, Folkins and Miller⁽²⁾ have recently published the free energy equations of formation for some seventy-seven hydrocarbons and others. The present author, with the aid of the mentioned literature, along with various other published data⁽⁵⁾ as of Thomas, Egloff and Morrell, Rossini and Pitzer, has derived simple free energy equation for the isomerization reactions and computed the free energy changes at 0°, 25°, 100°, 200° and 300°C.

The free energy equations were derived in the form of:

$$\Delta F^\circ = A+BT\,, \qquad (7)$$

where A's and B's are constants.

From such a simple relationship for ΔF° as a function of temperature, we may grasp very easily the change of free energy at any temperature, i.e., the thermodynamical possibility of various isomerization reactions important in the field of industrial synthesis. Table 1 gives these free energy equations as well as ΔF's at various temperatures. Table 2 shows the comparison of ΔF's at 298.16°K. between our calculations and those of other sources available. Table 3 compiles the ΔF°'s for various important hydrocarbons in order to show how they differ from those data compiled and selected by different authors, for the sake of thoroughness.

Discussions. In examining the tables, we find that the reactions as written are seen very definitely to be more favourable if the temperature is lower i.e., the lower the temperature, the more favourable the reaction from the left to right is, except for a few as Nos. 11, 16, 17, 19, 35, 47, which are easily seen in the table. In the reaction, *n*-butane=isobutane, at 200°C., ΔF° is found to be positive, while in the case of *n*-pentane=isopentane, even at 300°C., ΔF° is still negative. In the case of *n*-pentane=tetramethylmethane even at 200°C., ΔF° is already a

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(5) (a) Thomas, Egloff and Morrell, *Ind. Eng. Chem.*, **29**(1937), 1260.
(b) F. D. Rossini, *Chem. Rev.*, **27**(1940), 1–15.
(c) K. S. Pitzer, *Chem. Rev.*, **27**(19140), 39–57.

positive quantity. The formation of neohexane shows positive ΔF° at 200°C., while by alkylation of isobutane to get neo-hexane it is found to be thermodynamically very much favourable. As regards the transformation between dimethylated compounds, as 2,2-dimethylbutane=2,3-dimethylbutane, ΔF° favours the reaction if carried over at a higher temperature. The same is true in the case of

$$\left.\begin{array}{l}\text{2,2-dimethylpentane}\\ \\ \text{3,3-dimethylpentane}\end{array}\right\} = \left\{\begin{array}{l}\text{2,3-dimethylpentane}\\ \\ \text{2,4-dimethylpentane}\end{array}\right.$$

$$\left.\begin{array}{l}\text{2,2-dimethylpentane}\\ \\ \text{3,3-dimethylpentane}\end{array}\right\} = \left\{\begin{array}{l}\text{2-methylhexane}\\ \text{3-methylhexane}\\ \text{3-ethylpentane}\end{array}\right.$$

and few others already mentioned. In the case of tri- or tetra-methylated compounds, the decreasing of ΔF°'s was found to be more or less at a lower temperature. *n*-heptane and methylated heptane or *n*-octane seem to be very easily transformed to more complicated and branched compounds over wide ranges of temperature as illustrated in 2-methylheptane, 3-methylheptane and 4-methylheptane, respectively, going over to 2,2,3,3-tetramethylbutane, as well as *n*-heptane into 2-methylhexane, 3-methylhexane and 3-ethylpentane etc. These facts seem very reasonable as compared with the fact that *n*-heptane, in the presence of chromium oxide gel catalyst, easily is converted to toluene, by the cyclization process(6).

P. F. Bruins and J. D. Czarnecki(7) recently published a very interesting paper in connection with the relation between structure and free energy of organic molecules and proposed empirically, so-called "Bond Free Energy Equation". The idea of this bond free energy equation is very suggestive as well as very practicable and convenient to some extent in the calculation of free energy for the reactions in the engineering purpose. As they called attention to the relation between structure and free energy values, some possible and useful correlation may be obtained if the structure of these hydrocarbons and bond free energy are considered; for instance such reaction as isopentane=tetramethylmethane (neopentane), of which the skeleton structure can be represented as:

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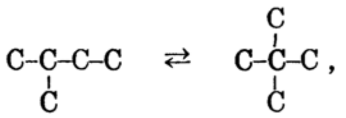
(6) S. G. Goldwasser and H. S. Taylor, *J. Am. Chem. Soc.*, **61** (1939), 1766–1769; S. Kinumaki, N. Kawatake and Asakura, "Nippon Gakujutsu Kyokai," Report No. 16 (1941), 52–54; D. J. Salley, H. Fehrer and H. S. Taylor, *J. Am. Chem. Soc.* **63** (1941), 1131–1133; J. D. Turkevich, H. Fehrer and H. S. Taylor, *J. Am. Chem. Soc.*, **63** (1941), 1129–1131; H. S. Taylor and J. Turkevich, *Trans. Faraday Soc.*, **35** (1939), 921.

(7) P. F. Bruins and J. D. Czarnecki, *Ind. Eng. Chem.*, **33** (1941), 201–203.

(8) (C–CH_3) type bond, according to Bruins and Czarnecki, was introduced instead of finding the correction factors for C–C, and C–H type bonds as influenced by various substitutions.



$$\mathrm{C{-}\underset{\displaystyle C}{\underset{|}{C}}{-}C{-}C} \rightleftarrows \mathrm{C{-}\overset{\displaystyle C}{\overset{|}{\underset{\displaystyle C}{\underset{|}{C}}}}{-}C},$$

where in isopentane, $3(C{-}CH_3)$(8), $1(C{-}C)$, $12(C{-}H)$ bonds and in tetramethylmethane, $4(C{-}CH_3)$, $12(C{-}H)$ bonds are involved. Therefore from the concept of Bond Free Energy Equation, ΔF° for isomerization can be represented roughly as:

$$\Delta F_{3(C-CH_3)}+\Delta F_{1(C-C)}+\Delta F_{12(C-H)}+\delta F_i^\circ = \Delta F_{4(C-CH_3)}+\Delta F_{12(C-H)}\,.$$

Therefore, $$\delta F_i^\circ = \Delta F_{1(C-CH_3)}-\Delta F_{1(C-C)} \qquad (8)$$

but more elaborately speaking, it should be

$$\delta F_i^{\circ\prime} = \Delta F_{1(C-CH_3)}-\Delta F_{1(C-C)}+\Delta F_{3(C-H)}{}'-\Delta F_{2(C-H)}{}''-\Delta F_{1(C-H)}{}'''. \qquad (9)$$

This can be seen from the comparision of the data from (8) and $\Delta F^\circ = -2739+7.1T$ respectively, -13166 cal. and -623 cal. (Considerable difference). Therefore the difference in these values is probably due to the fact that the term(9) $(3(H{-}H)^{I}-2(C{-}H)^{II}-(C{-}H)^{III})$ is neglected, in other words, using these bond free energy equations, differentiation between $(C{-}H)^{I}$, $(C{-}H)^{II}$ and $(C{-}H)^{III}$ should be borne in mind. Otherwise, the agreement between such calculations cannot be expected. This does not mean that the idea of Bond Free Energy Equation is useless, but it only shows that Bond Free Energy Equation must be so refined for different types of bonds as modified and influenced by various substitutions of the groups. At any rate, such calculation carried out in Bond Free Energy Equation, may be useful at least for the engineering purpose, as the types of calculations illustrated in Bruins and Czarnecki's publication.

As observed in the values of ΔF°'s at various temperatures, the free energy changes involved in the isomerization reactions are of small magnitude, and as already stated, the errors involved are sometimes as big as the ΔF° itself(10). Therefore, before we get any definite conclusion, more refined and accurate data must be obtained. Though the present situation may not give a precise conclusion, the general trend of, and aspects of isomerization reaction with a special reference to their thermodynamical possibility may be grasped; at least, the relative changes in the possibility of transformation with respect to the variation of temperature, which is one of the most important factors, may be ascertained.

The free energy equations for some of the useful reactions such as the formation of neohexane from the alkylation of isobutane, and the formation of 2,2,4-trimethylpentane (isooctane) from the coupling of isobutene and isobutane are also derived and ΔF°'s for these reactions also are shown.

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(9) Probably other factors also may be responsible for these discrepancies (such as (C–C) bond etc.).

(10) E. Wilson, *Chem. Rev.*, **21** (1937), 129–167.

Table 1. Equations for Free Energies of Isomerization Reactions as a Function of Temperature.

	Reactions	Free Energy Equations $\Delta F^\circ = A+BT$		ΔF° cal./mol.				
		A	B	0°	25°	100°	200°	300°
1	*n*-Butane=Isobutane	− 1635	+ 4.0	− 543	− 443	− 143	+ 257	+ 657
2	*n*-Pentane=Isopentane	− 1932	+ 2.8	− 1167	− 1097	− 887	− 607	− 327
3	*n*-Pentane=Tetramethylmethane	− 4671	+ 9.9	− 1967	− 1720	− 977	+ 13	+ 1003
4	Isopentane=Tetramethylmethane	− 2739	+ 7.1	− 800	− 623	− 90	+ 620	+ 1330
5	*n*-Hexane=2,2-Dimethylbutane (Neohexane)	− 4650	+11.1	− 1619	− 1341	− 509	+ 601	+ 1711
6	Isobutane+C_2H_4=2,2-Dimethylbutane (Neohexane) $\Delta F^\circ = -25178+2.303\times 2.72 T\log T - 19.55\times 10^{-2}T^2+12.94T$			−18934	−18437	−17060	−15505	−14281
7	*n*-Hexane=2,3-Dimethylbutane	− 3550	+ 8.0	− 1365	− 1165	− 565	+ 235	+ 1035
8	*n*-Hexane= 2-Methylpentane 3-Methylpentane	− 1750	+ 4.0	− 658	− 558	− 258	+ 142	+ 542
9	2-Methylpentane 3-Methylpentane =2,2-Dimethylbutane	− 2900	+ 7.1	− 961	− 783	− 251	+ 459	+ 1169
10	2-Methylpentane 3-Methylpentane =2,3-Dimethylbutane	− 1800	+ 4.0	− 708	− 608	− 308	+ 92	+ 492
11	2,2-Dimethylbutane=2,3-Dimethylbutane	+ 1100	− 3.1	+ 253	+ 176	− 57	− 367	− 677
12	*n*-Heptane= 2,2-Dimethylpentane 3,3-Dimethylpentane	− 4710	+ 9.7	− 2061	− 1818	− 1091	− 121	+ 849
13	*n*-Heptane= 2,3-Dimethylpentane 2,4-Dimethylpentane	− 3610	+ 6.6	− 1808	− 1643	− 1148	− 488	+ 172
14	*n*-Heptane= 2-Methylhexane 3-Methylhexane 3-Ethylpentane	− 1810	+ 2.6	− 1100	− 1035	− 840	− 580	− 320
15	*n*-Heptane=2,2,3-Trimethylbutane	− 6510	+13.7	− 2769	− 2426	− 1399	− 29	+ 1341
16	2,2-Dimethylpentane 3,3-Dimethylpentane = 2,3-Dimethylpentane 2,4-Dimethylpentane	+ 1100	− 3.1	+ 253	+ 176	− 57	− 367	− 677
17	2,2-Dimethylpentane 3,3-Dimethylpentane = 2-Methylhexane 3-Methylhexane 3-Ethylpentane	+ 2900	− 7.1	+ 961	+ 783	+ 251	− 459	− 1169
18	2,2-Dimethylpentane 3,3-Dimethylpentane =2,2,3-Trimethylbutane	− 1800	+ 4.0	− 708	− 608	− 308	+ 92	+ 492

Table 1.—(*Continued*)

	Reactions	Free Energy Equations $\Delta F^\circ = A+BT$		ΔF° cal./mol.				
		A	*B*	0°	25°	100°	200°	300°
19	2,3-Dimethylpentane 2,4-Dimethylpentane = 2-Methylhexane 3-Methylhexane 3-Ethylpentane	+ 1800	− 4.0	+ 708	+ 608	+ 308	− 92	− 492
20	2,3-Dimethylpentane 2,4-Dimethylpentane = 2,2,3-Trimethylbutane	− 2900	+ 7.1	− 961	− 783	− 251	+ 459	+ 1169
21	3-Methylhexane 2-Methylhexane 3-Ethylpentane = 2,2,3-Trimethylbutane	− 4700	+11.1	− 1669	− 1391	− 559	+ 551	+ 1661
22	*n*-Octane = 2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane	− 1770	+ 4.0	− 678	− 578	− 278	+ 122	+ 522
23	*n*-Octane = 3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane	− 4670	+11.1	− 1639	− 1361	− 529	+ 581	+ 1691
24	*n*-Octane = 2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane	− 3570	+ 8.0	− 1385	− 1185	− 585	+ 215	+ 1015
25	*n*-Octane=2,3,4-Trimethylpentane	− 5470	+12.0	− 2193	− 1893	− 993	+ 207	+ 1407
26	*n*-Octane = 2,2,3-Trimethylpentane 2,3,3-Trimethylpentane	− 6470	+15.1	− 2346	− 1969	− 836	+ 674	+ 2184
27	*n*-Octane=2,2,4-Trimethylpentane	− 6470	+12.8	− 2974	− 2654	− 1694	− 414	+ 866
28	*n*-Octane=2,2,3,3,-Tetramethylbutane	− 9370	+22.2	− 3307	− 2752	− 1087	+ 1133	+ 3353
29	2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane = 3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane	− 2900	+ 7.1	− 961	− 783	− 251	+ 459	+ 1169

Table 1.—(*Continued*)

	Reactions	Free Energy Equations $\Delta F^\circ = A+BT$		ΔF° cal./mol.				
		A	*B*	0°	25°	100°	200°	300°
30	2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane = 2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane	− 1800	+ 4.0	− 708	− 608	− 308	+ 92	+ 492
31	2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane = 2,3,4-Trimethylpentane	− 3600	+ 8.0	− 1415	− 1215	− 615	+ 185	+ 985
32	2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane = 2,2,3-Trimethylpentane 2,3,3-Trimethylpentane	− 4700	+11.1	− 1669	− 1391	− 559	+ 551	+ 1661
33	2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane = 2,2,4-Trimethylpentane	− 4700	+ 8.8	− 2297	− 2077	− 1417	− 537	+ 343
34	2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane = 2,2,3,3-Tetramethylbutane	− 7600	+18.2	− 2630	− 2175	− 810	+ 1010	+ 2830
35	3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane = 2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane	+ 1100	− 3.1	+ 253	+ 176	− 57	− 367	− 677

Table 1.—(*Continued*)

	Reactions	Free Energy Equations $\Delta F^\circ = A+BT$		ΔF° cal./mol.				
		A	B	0°	25°	100°	200°	300°
36	3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane =2,3,4-Trimethylpentane	− 700	+ 0.9	− 454	− 432	− 364	− 274	− 184
37	3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane =2,2,3-Trimethylpentane 2,3,3-Trimethylpentane	− 1800	+ 4.0	− 708	− 608	− 308	+ 92	+ 492
38	3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane =2,2,4-Trimethylpentane	− 1800	+ 1.7	− 1336	− 1293	− 1166	− 996	− 826
39	3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane =2,2,3,3,-Tetramethylbutane	− 4700	+11.1	− 1669	− 1391	− 559	+ 551	+ 1661
40	2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane =2,3,4-Trimethylpentane	− 1800	+ 4.0	− 708	− 608	− 308	+ 92	+ 492
41	2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane =2,2,3-Trimethylpentane 2,3,3-Trimethylpentane	− 2900	+ 7.1	− 961	− 783	− 251	+ 459	+ 1169

Table 1.—(*Concluded*)

	Reactions	Free Energy Equations $\Delta F° = A+BT$		$\Delta F°$ cal./mol.				
		A	B	0°	25°	100°	200°	300°
42	2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane =2,2,4-Trimethylpentane	− 2900	+ 4.8	− 1589	− 1469	− 1109	− 629	− 149
43	2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane =2,2,3,3-Tetramethylbutane	− 5800	+14.2	− 1922	− 1567	− 502	+ 918	+ 2338
44	2,3,4-Trimethylpentane = {2,2,3-Trimethylpentane 2,3,3-Trimethylpentane}	− 1100	+ 3.1	− 253	− 176	+ 57	+ 367	+ 677
45	2,3,4-Trimethylpentane =2,2,4-Trimethylpentane	− 1100	+ 0.8	− 882	− 862	− 802	− 722	− 642
46	2,3,4-Trimethylpentane =2,2,3,3-Tetramethylbutane	− 4000	+10.2	− 1214	− 959	− 194	+ 826	+ 1846
47	2,2,3-Trimethylpentane 2,3,3-Trimethylpentane =2,2,4-Trmethylpentane	0	− 2.3	− 628	− 686	− 858	− 1088	− 1318
48	2,2,3-Trimethylpentane 2,3,3-Trimethylpentane =2,2,3,3-Tetramethylbutane	− 2900	+ 7.1	− 961	− 783	− 251	+ 459	+ 1169
49	2,2,4-Trimethylpentane =2,2,3,3-Tetramethylbutane	− 2900	+ 9.4	− 333	− 98	+ 607	+ 1547	+ 2487
50	Isobutene+Isobutane=2,2,4-Trimethylpentane (isooctane) $\Delta F° = -21965 + 5.435 T \log T - 0.25 \times 10^2 T^2 + 24.4T$			−11871	−10906	− 7994	− 4103	− 211

Table 2. Comparison of the ΔF°'s for Isomerization Reaction at 25°C.***

Reactions	ΔF°			
	Wilson*	Hamai	Knowlton(17) Rossini	Pitzer(22)
n-Butane = Isobutane	− 140(11) − 820 (l.)(14b)	− 443 (g.)		− 530 (g.)
Butene-1 = Isobutene	−2540(12)	−2396 (g.)		−2370 (g.)
Butene-1 = Cis-butene-2	−1920(13)	−1234 (g.)		−1240 (g.)
Butene-1 = Trans-butene-2	−2330(14)	−2006 (g.)		−2010 (g.)
Cis-butene-2 = Trans-butene-2	− 410(15)	− 771 (g.)		− 770 (g.)
Cis-butene-2 = Isobutene	− 620(16)	−1161 (g.)		−1130 (g.)
Trans-butene = Isobutene		− 390 (g.)		− 360 (g.)
n-Pentane = 2-Methylbutane (isopentane)	− 100 (l.)(20) −1020 (l.)(19b)	−1097 (g.)	−1095 (g.)** ($\Delta E = -1930 \pm 260$)	−1570 (g.)
n-Pentane = 2,2-Dimethyl-propane (Tetramethyl-methane) (Neopentane)	+ 270 (g.)(20)	−1720 (g.)	−1728 (g.)** ($\Delta E = -4680 \pm 310$)	−1690 (g.)
2-Methyl-butane (isopentane) = 2,2-Dimethyl-propane		− 623 (g.)	− 633 (g.)** ($\Delta E = -2750 \pm 270$)	− 120 (g.)

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* E. Wilson, *Chem. Rev.*, **21** (1937), 129–167.

** Calculated by the present author from ΔE's of Rossini.

*** Those data for the unsaturated compounds are from our report II to be published immediately after I.

(11) Arbutzov, *Ber.*, **67**B (1934), 563, 569.

(12) Aschân, *Ann.*, **324** (1902), 12.

(13) Aston and Messerly, *J. Am. Chem. Soc.*, **58** (1936), 2354.

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(15) Barrett and Linstead, *J. Chem. Soc.*, (1936), 611.

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Table 2.—(*Concluded*)

Reactions	ΔF°			
	Wilson*	Hamai	Knowlton(17) Rossini	Pitzer(22)
n-Hexane = 2-Methylpentane		−558 (g.)	−1061+230 (g.)	−1080 (g.)
n-Hexane = 3-Methylpentane		−558 (g.)	−352+230 (g.)	
n-Hexane = 2,3-Dimethylbutane		−1165 (g.)	−796+230 (g.)	
n-Hexane = 2,2-Dimethylbutane		−1341 (g.)	−2385+230 (g.)	−2380 (g.)
Hexene-1 = Cyclohexane	−8100			
Hexene-1 = Methylcyclopentane	−12200			
Cyclohexane = Methylcyclopentane	−4100			
	+1150 (l.)(21)			+970 (l.)(19b)
n-Heptane = 2-Methylhexane	−1520 (l.)	−1035 (g.)		−1150 (g.)
n-Heptane = 3-Methylhexane	−1120 (l.)	−1035 (g.)		
n-Heptane = 3-Ethylpentane	−320 (l.)	−1035 (g.)		
n-Heptane = 2,2-Dimethylpentane	−320 (l.)	−1818 (g.)		−2050 (g.)
n-Heptane = 2,3-Dimethylpentane	−620 (l.)	−1643 (g.)		
n-Heptane = 2,4-Dimethylpentane	+180 (l.)	−1643 (g.)		
n-Heptane = 3,3-Dimethylpentane	+920 (l.)	−1818 (g.)		
n-Heptane = 2,2,3-Trimethylbutane	+680 (l.)	−2426 (g.)		
Heptene-1 = Methylcyclohexane	−15450 (l.)			
Heptene-1 = 1,2-Dimethyl cyclopentane	−18050 (l.)			
n-Octane = 2,2,4-Trimethylpentane	+80 (l.)			
	+2230 (l.)**	−2654 (g.)		−2700 (g.)
n-decane = 2-Methyl-nonane			−1490+670 (l.)(18)	
n-Decane = 5-Methylnonane			−1300+600 (l.)(18)	

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(**) Based on the old data of *n*-octane (E. Wilson).

Table 3. Comparison of Thermodynamic Constants for the Formation of Gaseous Hydrocarbons.

at 298.1 °K (n C (graphite) + m H_2 (g.) = C_nH_{2m} (g.))

Substances	ΔS (Pitzer) cal/deg.	ΔH (Pitzer) K.cal.	ΔF° K.cal. Pitzer	ΔF° K.cal. Thacker and Others	ΔF° K.cal. Egloff	ΔF° K.cal. Wilson
Methane	− 19.39	−17.865 ± 0.074	−12.085	−12.134	−12.300 (−12.340)	
Ethane	− 41.61	−20.191 ± 0.108	− 7.787	− 7.784	− 8.260 (− 8.730)	
Propane	− 64.4	−24.750 ± 0.124	− 5.55	− 5.576	− 6.220 (− 7.380)	
n-Butane	− 87.5	−29.715 ± 0.153	− 3.63	− 3.748	− 5.000 (− 6.450)	−4.580 (g.) −5.000 (g.) new data
Isobutane	− 91.2	−31.350 ± 0.132	− 4.16	− 4.190	− 4.900 (− 6.850)	−4.720 (g.) −4.900 (g.) new data
n-Pentane	−111.1	−34.739 ± 0.213	− 1.62	− 1.617	− 2.570	−2.570 (g.) −2.820 (l.) −8.600 (l.) old data
2-Methylbutane	−112.3	−36.671 ± 0.153	− 3.19			−2.920 (l.)
Tetramethylmethane	−121.1	−39.410 ± 0.227	− 3.31	− 3.337	− 4.500 (− 6.670)	
n-Hexane	−134.5	−40.01 ± 0.50	+ 0.08	− 0.392	− 1.500	−7.000 (l.)
2-Methylpentane	−136.8	−41.8 ± 0.7	− 1.0	− 0.950		
2,2-Dimethylbutane	−141.2	−44.4 ± 0.7	− 2.3	− 1.733		
n-Heptane	−158.0	−45.35 ± 0.80	+ 1.75	+ 1.482	+ 0.190	−1.480 (l.), (new data) −3.000 (l.)
2-Methylhexane	−160.1	−47.1 ± 1.00	+ 0.6	+ 0.447	− 1.300	−3.000 (l.)
2,2-Dimethylpentane	−166.2	−49.8 ± 1.0	− 0.3	− 0.337	− 0.130	−1.800 (l.)
n-Octane	+181.5	−50.70 ± 1.0	+ 3.4	+ 2.518	+ 1.520	−0.850 (l.) (−3.000) +1.520 (g.)
2,2,4-Trimethylpentane	−190.8	−56.2 ± 2.0	+ 0.7	− 0.136	+ 1.570	−0.770 (l.)
n-(C_nH_{2n+2}) ($n > 6$)	− 23.49 n +6.4	−(5.35 n−7.90) ±0.12 n	(+1.65 n −9.80)			
Ethylene	− 12.49	+12.556 ± 0.067	+16.279	+16.339	+15.820 (15.530)*	
Propylene	− 32.8	+ 4.956 ± 0.110	+14.73	+14.820	+14.820 (13.920)	
1-Butene	− 55.1	+ 0.383 ± 0.181	+16.81	+17.041	+16.780 (15.330)	
Cis-2-butene	− 56.9	− 1.388 ± 0.181	+15.57	+15.806	+14.860 (14.170)	
Trans-2-butene	− 57.5	− 2.338 ± 0.181	+14.80	+15.035	+14.450 (13.400)	
Isobutene (2-Methylpropene)	− 59.2	− 3.205 ± 0.162	+14.44	+14.645	+14.240 (13.020)	
Acetylene	+ 14.07	+54.228 ± 0.233	+50.034		+50.840 (49.600)	

(*) Spectroscopic data, assuming free rotation of the C—C bonds (Egloff).

Conclusion. Thus far we have derived the free energy equations of isomerization reactions of the saturated hydrocarbons as a function of temperature and calculated ΔF°'s at various temperatures. They serve to indicate to some extent the general trend of the ΔF°'s values with structural changes. Some correlation and discussion with the so-called "Bond Free Energy Equation" are presented with certain restrictions. Those calculated free energy values for the isomerization from our simple derived equations have been found to give satisfactory results as compared with those given by various authors as K. S. Pitzer, F. D. Rossini, as well as E. Wilson, and some experimental evidences.

Parks and Huffman(23), in 1932, were led to the conclusion that any branched isomer should be on a higher free energy level than the normal compound; while Knowlton and Rossini's data(19)(20) have given that just the reverse is true. The situation stimulated such investigators as Montgomery, McAteer and Franke(24) and others to study the isomerization reactions and all these results led to the conclusion supported by Rossini. Our calculations also support that such conclusion is more reasonable.

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