in Figs. 2 and 3 above, a function of the ionic charge and of the position in the periodic system. The writers have tried to establish a more complete picture by taking into consideration the size of the ions. Very little information is available on actual ionic radii determination. However, qualitatively we know that ions at the top of the group are most strongly hydrated, and little hydration is noted as the shielding effect of the electronic orbits increases. The series of hydrated ionic radii is just the reverse of the crystalline or gaseous ion radii. Remy[11] arrived at ionic radii values from mobility determinations. We have plotted the so-obtained hydrated ionic radii values against the equilibrium exchange and have found a very simple relationship between the two quantities as shown in Fig. 4.

All values of ions of the first group fall on a straight line and the same holds for the ions of the second group. The slope is the same for both groups indicating that ionic size really determines the relative accessibility of an exchange group. The shift of the two lines indicates the "charge effect."

The two curves may be interpreted by a universal equation, to correlate exchange capacity, hydrated ionic radius and valence. We have written the equation common to both curves

$$R = \alpha \times 28.3 \times \text{E.E.} + \beta(23.5 + 5.5V)$$

where R represents the hydrated ionic radius from Remy's data, E.E. the equilibrium exchange in meq./g., V the valence of the entering ion, and α and β are proportionality constants for each exchanger type, and are unity for the case of a sulfonated coal type cation exchange under the experimental conditions employed. Similar efforts to correlate valence and exchange were made by Gapon,[12] however not from the viewpoint or introducing the ion size in the exchange equation.

Acknowledgment.—The authors wish to express thanks to Calvin Calmon, Paul C. Goetz, Marvin Lane, Sidney Sussman, Howard L. Tiger and Harold F. Walton for helpful criticisms and suggestions.

Summary and Conclusions

1. Additional rate determinations have been carried out, showing the effects of both anions and cations on the rates of cation exchange reactions.
2. If the cation is kept constant, but the anion is varied in a series of H^+ ion exchange experiments, the rate of approach of equilibrium exchange is the same but the values obtained with salts of weak acids are very much larger as contrasted with strong acid salts.
3. The cation exchange capacity increases as function of the charge of the cation; however, the monovalent ions exchange with faster rate than the divalent ions. Within a group, the ion in the lower part of the group exchanges faster and has a higher equilibrium exchange; at the end of the group the differences are less pronounced.
4. The variation of rate constants among the cations is generally what one would expect from their respective diffusion rates. However, the correlation is not ideal. So, *e. g.*, the ratio of ionic mobilities for K:Li, which ought to be the same as the ratio of their diffusion rates, is 1.9:1 while the ratio of the respective exchange rate was found to be 1.5:1. Thus, diffusion alone is not the rate determining factor but other effects, such as ionic size, charge, and steric availability of the exchange position in the exchanger play a decided role.
5. The equilibrium exchange for a series of ions in one group is a function of their size, *i. e.*, the hydrated ionic radius or volume, and a simple graphical relationship is pointed out which can be brought into a linear equation.

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[11] H. Remy, *Z. physik. Chem.*, **89**, 467, 483 (1915); *cf.* also H. Jenny, *Kolloid Beihefte*, **23**, 428 (1927); *J. Phys. Chem.*, **36**, 2217 (1932); G. Wiegner and H. Jenny, *Kolloid-Z.*, **42**, 268 (1927).

[12] E. N. Gapon, *J. Gen. Chem.* (U. S. S. R.), **13**, 382 (1943).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Determination of Equilibrium Constants for Butanes and Pentanes

BY HERMAN PINES, BRUNO KVETINSKAS, LOUIS S. KASSEL AND V. N. IPATIEFF

In recent years, several papers on the isomerization equilibrium constants of butanes[1,2] and pentanes[3] have appeared. Most of the work is open to criticism, however, because of the fact that the isomerization was accompanied by excessive decomposition which even became the predominant reaction in extreme cases. In the present investigation, the equilibrium constants were established by studying the isomerization from both the normal and the isoparaffin side, within wide temperature ranges and under experimental conditions designed to reduce to a minimum the amount of secondary reactions. Depending upon the temperature level investigated, the experiments were carried out in sealed tubes, a stirring autoclave, or a continuous flow type apparatus.

Experimental Methods

The catalysts used consisted of aluminum bromide or aluminum chloride, the latter usually deposited on a car-

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[1] B. Moldavskii and T. Nizovkina. *J. Gen. Chem.* (U. S. S. R.), **9**, 1652 (1939).

[2] G. C. A. Schuit, H. Hoog, and J. Verheus, *Rec. trav. chim.*, **59**, Nos. 7–8, 793–810 (1940).

[3] B. Moldavskii, T. Nizovkina and R. A. Shterner, *J. Gen. Chem.* (U. S. S. R.), **10**, 1183 (1940).

rier. In some instances, a catalyst composed of aluminum chloride–metal halide was used which possessed a high isomerizing activity but caused very little decomposition at elevated temperatures. All of the experiments in which aluminum chloride-containing catalysts were used were made in the presence of hydrogen chloride. In order to avoid the formation of undesirable products during isomerization, especially at elevated temperatures, it was found necessary that the contact time between the catalyst and the hydrocarbon be relatively short. This was made possible by using a flow-type apparatus. In the case of pentanes, hydrogen was added to inhibit side reaction.

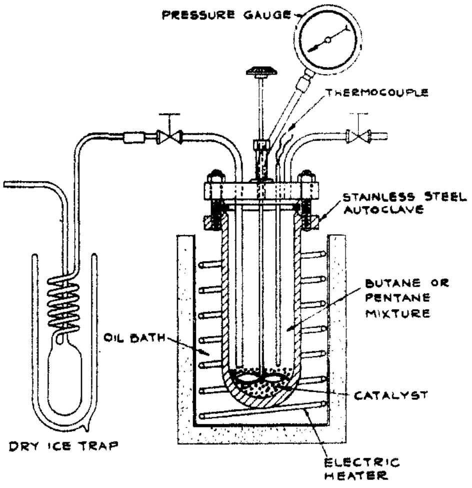

Fig. 1.—Batch apparatus for isomerization of butane or pentane.

The isomerization experiments were made in such a manner as to arrest the reaction at the studied temperatures of isomerization. This was accomplished by removing the catalyst from the product immediately after leaving the reaction zone or by arresting the activity of the isomerizing catalyst by sudden chilling to −76°.

The composition of the product resulting from isomerization was determined by distillation on a low-temperature Podbielniak apparatus. The efficiency of the distillation was determined from time to time by interjecting synthetic samples having composition approximating the equilibrium mixture of the hydrocarbons studied. The analytical results were accurate within ±0.8%.

Batch-Type Apparatus.—A batch-type apparatus (Fig. 1) consisting of a one-liter capacity, stainless steel pressure autoclave equipped with an electrically driven stirrer was employed to determine the equilibrium of pentanes at 65° and of butanes at 100°. The catalyst was sealed in the autoclave, which was then evacuated before the hydrocarbons and hydrogen chloride were charged. In the case of pentanes, hydrogen was added to bring the pressure to 20 atmospheres. The desired temperature was maintained by means of an electrically heated oil-bath. After stirring for a sufficient interval of time, a sample was drawn off (while still at the proper temperature) into a trap cooled with Dry Ice and acetone, through a tube reaching below the liquid level in the autoclave. The sample was washed with sodium hydroxide, dried with calcium chloride, and analyzed.

Continuous Flow-Type Apparatus.—A flow diagram of the apparatus used for determining the equilibrium of pentanes at 150 and 200° is shown in Fig. 2. In order to be certain that the catalyst was placed in a position having the least variance of temperature, a heat distribution curve (Fig. 3) was made of the inside temperature and skin temperature when the center of the furnace block was at 150°. A detailed diagram of the furnace and reaction tube showing the position of the catalyst bed in relation to the furnace temperature is given in Fig. 4.

The pentane mixture was pumped through the catalyst bed while hydrogen chloride and hydrogen were passed in at definite rates through calibrated capillaries. A pressure controller automatically maintained a constant pressure. At the exit, the product passed through a train consisting of a sodium hydroxide scrubber, a liquid receiver, a calcium chloride drying tower, a Dry Ice and acetone-cooled trap, a wet-test meter, and a gas sampling bottle. The product in the liquid receiver was combined with the product condensable in the Dry Ice and acetone-cooled trap for analysis by low-temperature Podbielniak distillation. A pre-run long enough to flush the system completely was allowed before a sample was taken for analysis.

The equilibrium of butanes at 150° was studied using the same flow-type apparatus described for pentanes except that the hydrogen chloride was introduced by pumping it in with the butane mixture.

Results

Butane Equilibrium.—The equilibrium constant for butane isomerization was determined at 25, 100 and 150°.

Equilibrium Constant at 25°.—Samples consisting of aluminum bromide dissolved in a mixture of normal and isobutane were sealed in glass tubes and kept at 25°. After certain intervals of time, tubes were opened and the mix-

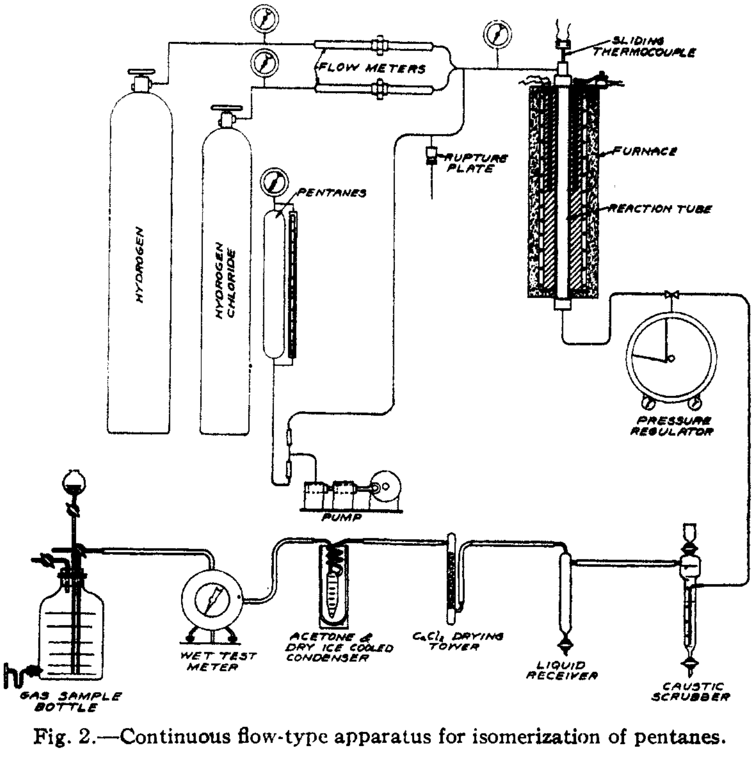

Fig. 2.—Continuous flow-type apparatus for isomerization of pentanes.

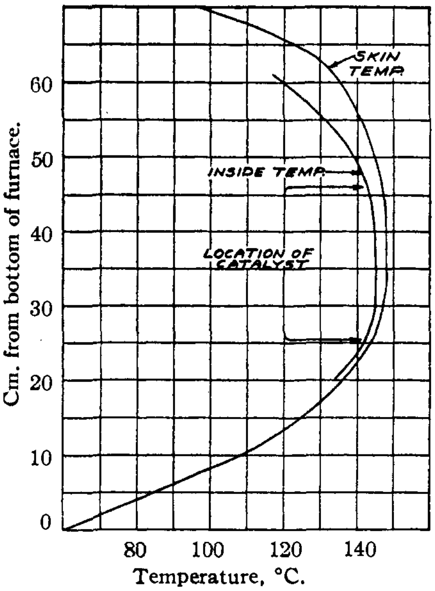

Fig. 3.—Temperature distribution curve for furnace of flow-type apparatus.

ture, after being washed with sodium hydroxide and dried, was analyzed. The experimental results are given in Table I. The reaction time in Expts. 1 and 3 was obviously insufficient to reach equilibrium. In Expts. 2 and 4, the butane fraction of the product contained 81.6% isobutane. This value is assumed to be the equilibrium composition for the liquid phase at 25°.

Equilibrium Constant at 100°.—The experiments were made in the batch-type apparatus, using aluminum chloride deposited on a carrier. The experimental data are given in Table II. Here again the shorter time was inadequate. At the longer contact times, the butane fraction in Expt. 6, in which equilibrium was approached from the normal butane side, contained 70.2% isobutane, while the butane fraction of Expt. 8, approaching equilibrium from the isobutane side, contained 72.3% isobutane. The average of these values, 71.2% isobutane, is taken as the equilibrium concentration in the liquid phase at 100°.

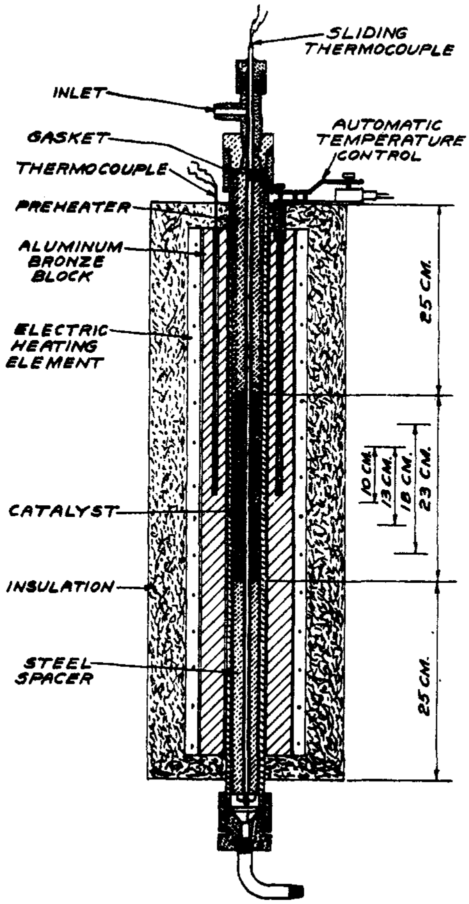

Fig. 4.—Furnace and reaction tube of flow apparatus.

Equilibrium Constant at 150°.—The reaction was carried out in a flow-type apparatus.

In order to reach equilibrium with a short contact time so as to prevent side reactions, a mixture of *n*-butane and isobutane, having a near equilibrium composition, was passed through a catalyst bed, composed of aluminum chloride deposited on

TABLE I

$n\text{-}C_4H_{10} \rightleftarrows i\text{-}C_4H_{10}$ AT 25°

Expt.	Reactant hydrocarbons Grams	% i-C_4H_{10}	% n-C_4H_{10}	$AlBr_3$, g.	Contact time, days	Analysis of prod., mole% C_3H_8	i-C_4H_{10}	n-C_4H_{10}	C_5H_{12}
1	49.2	90.1	9.9	19.4	37	...	85.7	14.3	
2	47.9	90.1	9.9	19.3	678	...	80.5	18.1	1.4
3	48.8	50.5	49.5	19.4	33	...	57.2	42.8	
4	48.9	50.5	49.5	19.2	670	0.3	80.2	18.1	1.4

TABLE II

$n\text{-}C_4H_{10} \rightleftarrows i\text{-}C_4H_{10}$ AT 100°

Expt.	Charge to autoclave % i-C_4H_{10}	% n-C_4H_{10}	C_4H_{10}, g.	HCl, g.	Catalyst, grams	Contact time, hr.	Analysis of prod., mole% C_3H_8	i-C_4H_{10}	n-C_4H_{10}	C_5H_{12}
5	0	100	114	5	30.0	4	0.4	30.6	67.5	1.5
6	50	50	118	5	53.2	21	...	68.7	29.2	2.1
7	100	0	110	4	54.2	4	...	96.9	2.1	1.0
8	85.7	14.3	134	5	54.0	25.5	1.4	68.8	26.4	3.4

a carrier. The results are given in Table III. The compositions of the butane fractions produced at the higher space velocities are 66.2 and 62.0% isobutane, the lower value corresponding to approach from the normal butane side. Corresponding values at the lower space velocities are 65.3 and 62.4%. The average of all four values is 64.0% isobutane, but the average of only the latter two, 63.8% isobutane, is believed to be a more reliable value for the equilibrium composition in the vapor phase at 150°.

TABLE III

n-C$_4$H$_{10}$ $\rightleftarrows$ i-C$_4$H$_{10}$ AT 150°[a]

Expt.	Butane mixture chgd. n-C$_4$H$_{10}$	i-C$_4$H$_{10}$	C$_5$H$_{12}$	Liq. space vel.	Analysis of prod., mole% C$_3$H$_8$	i-C$_4$H$_{10}$	n-C$_4$H$_{10}$	C$_5$H$_{12}$
9	69.3	30.4	0.3	1.1	0.8	65.5	33.5	0.2
10	69.3	30.4	.3	0.57	1.3	63.9	33.9	.9
11	52.2	47.4	.4	1.0	1.4	61.0	37.4	.2
12	52.2	47.4	.4	0.5	1.8	60.3	36.4	1.5

[a] The experiments were made at 99 atm. pressure using 4 mole % of hydrogen chloride based on butanes and 80 cc. of catalysts.

Pentane Equilibrium.—The equilibrium constant for pentane isomerization was determined at 65, 150 and 200°.

Equilibrium Constant at 65°.—The isomerization was made in the stirring autoclave in the presence of an aluminum halide–metal halide complex deposited on a carrier. Before the autoclave was heated, hydrogen was added to bring the pressure to 20 atmospheres, in order to eliminate side reactions. The experimental data are given in Table IV. On the basis of Experiments 13 and 14, it is concluded that the equilibrium mixture in the liquid phase consists of 87.2% of isopentane and 12.8% of n-pentane.

TABLE IV

n-C$_5$H$_{12}$ $\rightleftarrows$ i-C$_5$H$_{12}$ AT 65°

Expt.	Charge, i-C$_5$H$_{12}$	%[a] n-C$_5$H$_{12}$	Contact time, hours	Prod. mole% on C$_5$ basis i-C$_5$H$_{12}$	n-C$_5$H$_{12}$	% Decompn.
13	90	10	16.5	87.9	12.1	0.8
14	80	20	24.5	86.5	13.5	2.1
15	75	25	39.0	84.5	15.5	1.1
16	100	0	27.0	89.3	10.7	0.9

[a] In each experiment 80 g. of total pentanes, 35.5 g. of catalyst, and 9–10 g. of hydrogen chloride were used.

Equilibrium Constant at 150°.—The experiments were made in the flow-type apparatus at 39 atmospheres and in the presence of an aluminum chloride–metal halide complex deposited on a carrier. The experimental data are given in Table V.

In each experiment, 52 g. or 80 cc. of 8–12 mesh catalyst was used. The molar ratio of pentane, hydrogen chloride, and hydrogen used was 100:8.8:28.0. The liquid space velocity represents volume of liquid pentane at 20° passed per volume of catalyst per hour. On the basis of Expt. 18, Period 3 and Expt. 19, Period 2 it is concluded that the equilibrium mixture at 150° consists of isopentane 82.4% and n-pentane 17.6%. These experiments were made in a two-phase condition.

TABLE V

n-C$_5$H$_{12}$ $\rightleftarrows$ i-C$_5$H$_{12}$ AT 150°

Expt.	Period	Charge, i-C$_5$H$_{12}$	% n-C$_5$H$_{12}$	Liq. space vel.	Product mole% calculated on pentane basis i-C$_5$H$_{12}$	n-C$_5$H$_{12}$	Mole% decompn.
17	2	100	0	0.53	90.5	9.5	0.4
	3	100	0	.43	91.3	8.7	.6
18	2	90	10	.49	84.7	15.3	3.0
	3	90	10	.63	82.6	17.4	0.6
19	2	79.5	20.5	.47	82.3	17.7	1.0
	3	79.5	20.5	.38	82.2	17.8	1.0
20	2	75	25	.62	80.5	19.5	3.1
	3	75	25	.50	80.1	19.9	2.1

Equilibrium Constant at 200°.—The apparatus and procedure used were the same as that described for the experiments made at 150°. The catalyst employed was an aluminum chloride–metal halide complex deposited on a carrier. Catalysts of various compositions and many experimental conditions were tried in order to reach equilibrium with a minimum amount of decomposition. The most satisfactory results are given in Table VI. On the basis of Expts. 22 and 23, in which the charge compositions closely bracketed the equilibrium value, it is concluded that the equilibrium mixture contains 79.0% isopentane and 21.0% n-pentane. This value would not be significantly changed if Expt. 21 were included in the average.

TABLE VI

n-C$_5$H$_{12}$ $\rightleftarrows$ i-C$_5$H$_{12}$ AT 200°

Expt.	Charge, % i-C$_5$H$_{12}$	n-C$_5$H$_{12}$	Liquid space velocity	Product, mole% calculated on pentane basis i-C$_5$H$_{12}$	n-C$_5$H$_{12}$	Mole% decompn.
21	90	10	0.50	79.6	20.4	2.6
22	84	16	.33	80.7	19.3	1.9
23	75	25	.45	77.3	22.7	1.4

Discussion of Results

Isomerization of Butane.—It is desirable to reduce the experimental data to $K_G{}^0$, the vapor phase equilibrium constant at zero pressure. No phase equilibrium or P–V–T data on mixtures of normal and isobutane are available, but it is possible to use the data on the individual hydrocarbons with the assistance of plausible assumptions regarding the behavior of the mixture.

It is assumed that in liquid mixtures of normal and isobutane the fugacity of each component is equal to the fugacity of the pure material at the same temperature and pressure times the mole fraction of that component. It is further assumed that the fugacities of both components are equally affected by the minor amounts of dissolved catalysts, hydrogen chloride, and hydrogen. Then

$$K_G{}^0 = K_L \times \frac{f_I e^{(P-P_I)V_I/RT}}{f_N e^{(P-P_N)V_N/RT}}$$

where f_N, f_I are fugacities of liquid normal, and isobutane at temperature T, and at their respective vapor pressures P_N, P_I, V_N, V_I are the molar volumes of the liquids, and P is the total experimental pressure. Values of f_N and V_N are taken from the work of Sage, Webster and Lacey[4] and values of f_I and V_I from Sage and Lacey.[5] The values of V_N and V_I are so nearly the same that the correction factor is almost independent of the total pressure, P. At 110°, the factor changes by 1% for a change of about 18,000 mm. in P, and at lower temperatures it is even less sensitive. It is therefore considered sufficient to calculate K_G^0/K_L at the estimated total butane pressure without correction for other components. Values so obtained are shown in the first part of Table VII along with the vapor pressure ratios. It is clear that use of vapor pressures in Raoult's law would be unsatisfactory.

TABLE VII

ISOMERIZATION OF BUTANE

Temp., °C.	K_G^0/K_L	P_I/P_N	Mole% i-C_4H_{10} Liquid	Mole% i-C_4H_{10} Vapor
20	1.410	1.439	81.7	86.3
25	1.395	1.426	80.9	85.5
30	1.378	1.412	80.0	84.7
40	1.348	1.389	78.4	83.0
50	1.319	1.368	76.8	81.3
60	1.290	1.350	75.2	79.6
70	1.264	1.334	73.6	77.9
80	1.238	1.319	72.1	76.2
90	1.215	1.306	70.7	74.5
100	1.193	1.294	69.2	72.9
110	1.175	1.282	67.8	71.2
120				69.6
130				68.0
140				66.5
150				65.0

The vapor phase equilibrium constants are substantially independent of pressure. It is expected that K_G will be reduced as the pressure is increased, but approximate calculations suggest that the change cannot exceed 2% except for extremely high pressures attainable only above 150°. This correction is therefore ignored.

The summarized results of this work are compared with equilibrium determinations of Moldavskii and Nizovkina,[1] Montgomery, McAteer and Franke,[6] Schuit, Hoog and Verheus,[2] and Horne[7] in Table VIII and Fig. 5. The results of Schuit, *et al.*, are obviously wrong at 60°, and too discordant at 140° to receive serious consideration. Their value at 100° and all values of other observers agree within a maximum deviation of 3% in composition with values based on the equation

$$R \ln K_G^0 = (2318/T) - 4.250$$

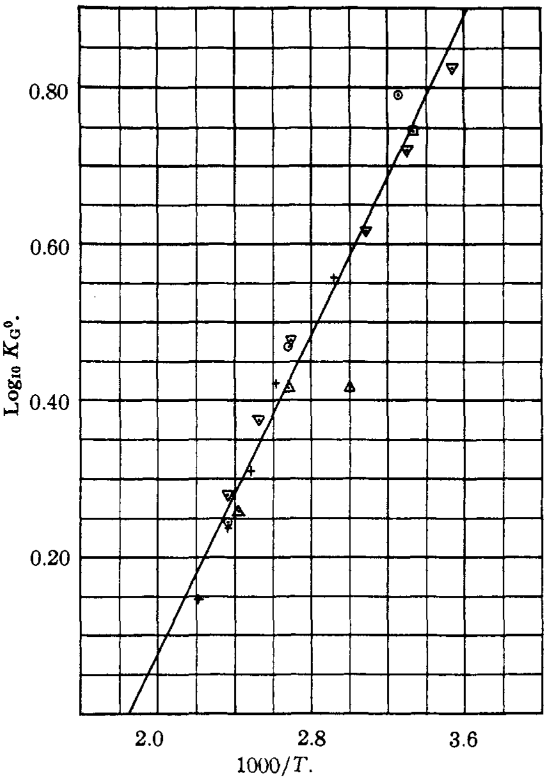

Fig. 5.—Experimental values of K_G^0 for isomerization of butane: ⊙, this work; +, Moldavskii, *et al.*; □, Montgomery, *et al.*; △, Schuit, *et al.*; ▽, Horne.

The corresponding value of 2318 cal./mole for the heat of isomerization of butane is markedly higher than the value of 1640 cal./mole determined by Rossini[8] from heats of combustion. The probable error of the value derived from equilibrium constants is less than 100 cal./mole, and there seems to be no doubt that the thermochemical value is incorrect. This same conclusion was reached previously by Frost[9] and by Messerly, Aston and Kennedy[10] as a result of calculations of the same character as those made here. The accumulation of additional equilibrium data has served merely to strengthen this conclusion.

The value of 4.25 e. u. for the entropy of isomerization is somewhat higher than the figure of 3.57 e. u. calculated by difference from the third-law values of Aston and Messerly[11] for normal butane and of Aston, Kennedy and Schumann[12] for isobutane, but the agreement is almost as good as could be expected, in view of estimated errors of

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(4) B. H. Sage, D. C. Webster and W. N. Lacey, *Ind. Eng. Chem.*, **29**, 1188 (1937).

(5) B. H. Sage and W. N. Lacey, *ibid.*, **30**, 673 (1938).

(6) C. W. Montgomery, J. H. McAteer and H. W. Franke, THIS JOURNAL, **59**, 1768 (1937).

(7) W. A. Horne, quoted in W. A. Gruse and D. R. Stevens, "Chemical Technology of Petroleum," 2nd ed., 1942, p. 446.

(8) F. D. Rossini, *Chem. Rev.*, **27**, 1 (1940).

(9) A. V. Frost, *J. Gen. Chem.* (U. S. S. R.), **9**, 1813 (1939).

(10) G. H. Messerly, J. G. Aston and R. M. Kennedy, THIS JOURNAL, **62**, 1630 (1940).

(11) J. G. Aston and G. H. Messerly, *ibid.*, **62**, 1917 (1940).

(12) J. G. Aston, R. M. Kennedy and S. C. Schumann, *ibid.*, **62**, 2059 (1940).

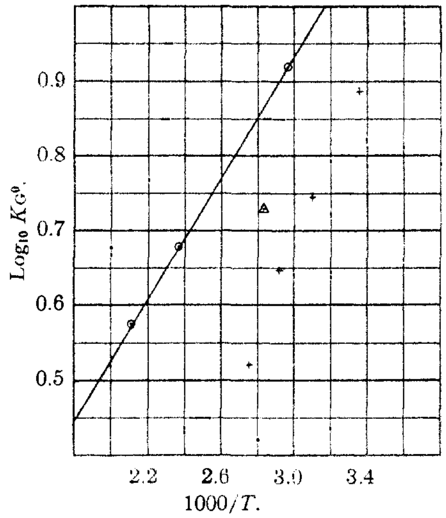

Fig. 6.—Experimental values of K_G^0 for isomerization of pentane: ⊙, this work; +, Moldavskii, *et al.*; △, Schuit, *et al.*

0.35 e. u. for the third-law value, and 0.25 e. u. for the value from equilibrium constants.

Calculated values for the mole % of isobutane at equilibrium are given in Table VII. It has not been considered desirable to tabulate extrapolated values. It is of interest to note, however, that at 500° $K = 0.53$ with an estimated uncertainty of 20%, and the equilibrium mixture contains (35 ± 4)% isobutane. The predominant occurrence of isobutane in products of catalytic cracking and destructive hydrogenation, therefore, must be interpreted in terms of reaction rates.

TABLE VIII

ISOMERIZATION OF BUTANE

Observer	Temp., °C.	Obs. K_G^0	Obs. phase	% Isobutane in observed phase Calcd.	Obs.			
This work	25	6.18	Liquid	80.8	81.3	81.6		
	100	2.95	Liquid	69.2	70.2	72.3		
	150	1.76	Vapor	65.0	62.4	65.3		
Moldavskii	70	3.61	Liquid	73.6	73.9	74.3		
	110	2.64	Vapor	71.2	71.7	73.4		
	130	2.04	Vapor	68.0	66.9	67.3		
	150	1.73	Vapor	65.0	63.1	63.8		
	180	1.41	Vapor	60.7	58.0	58.0	59.0	
Montgomery	27	5.55	Liquid	80.6	78	82		
Schuit	60	2.62	Liquid	75.2	64.5	66.3	67.6	68.4
	100	2.62	Liquid	69.2	67.1	67.9	69.0	71.2
	140	1.82	Vapor	66.5	60.4	62.3	64.5	69.6
Horne	10	6.69	Vapor	87.9	87.0	±1.0		
	30.3	5.25	Vapor	84.6	84.0	±0.8		
	52	4.13	Vapor	81.0	80.5	± .8		
	99	3.00	Vapor	73.0	75.0	±1.2		
	123	2.37	Vapor	69.1	70.3	±1.0		
	150	1.90	Vapor	65.0	65.5	±1.2		

Isomerization of Pentane.—The procedure used to convert K_L to K_G^0 is the same as for the butanes. The fugacities for liquid isopentane were calculated from the data of Young[13] and Young and Thomas[14]; values for normal pentane were taken from Sage and Lacey.[15] The final factors are given in the first part of Table IX.

TABLE IX

ISOMERIZATION OF PENTANE

Temp., °C.	K_G^0/K_L	P_I/P_N	Mole% i-C_5H_{12} Liquid	Vapor.
60	1.225	1.266	87.6	89.6
70	1.209	1.250	86.8	88.6
80	1.193	1.234	86.1	88.1
90	1.178	1.218	85.3	87.3
100	1.162	1.203	84.6	86.5
110	1.149	1.191	83.9	85.7
120	1.135	1.178	83.2	84.9
130	1.122	1.167	82.5	84.1
140	1.109	1.159	81.9	83.4
150	1.096	1.151	81.3	82.6
160				81.9
170				81.1
180				80.4
190				79.7
200				79.0

The runs made at 150° were probably in a two-phase region. Values of the vaporization equilibrium constants for this system are not known, but may be estimated as follows

n-C_5H_{12}	0.6843
i-C_5H_{12}	.7500
HCl	4.3
H_2	6.4

These estimates are based on data of Nelson and Bonnell[16] for hydrogen, and on data of Ottenweller, Holloway and Weinrich,[17] together with unpublished data from this laboratory for hydrogen chloride, with considerable extrapolation in both cases. The value for isopentane is the usual estimate, and the ratio of the values for the pentane isomers conforms to the requirement of Table IX. The calculated compositions of the two phases conforming to these values and the observed total composition are:

	Moles of Liquid	Vapor	Total
i-C_5H_{12}	13.589	68.811	82.400
n-C_5H_{12}	3.132	14.468	17.600
HCl	0.293	8.507	8.800
H_2	.633	27.367	28.000
	17.647	119.153	136.800

hence

$$K_L = 4.34$$
$$K_G = 4.76$$

The summarized results of this work are compared with equilibrium determinations of Schuit,

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[13] S. Young, *Proc. Phys. Soc.*, **13**, 602 (1895).

[14] S. Young and G. L. Thomas, *ibid.*, **13**, 658 (1895).

[15] B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.*, **34**, 730 (1942).

[16] E. E. Nelson and W. S. Bonnell, paper presented before the Petroleum Division, at the Buffalo meeting of the American Chemical Society, Sept. 7 to 11, 1942, p. 99.

[17] J. H. Ottenweller, C. Holloway, Jr., and W. Weinrich, *ibid.*, p. 121.

Hoog and Verheus[2] and of Moldavskii, Nizovkina and Shterner[3] in Table X. The large apparent errors in the older work are probably due mainly to excessive side reactions. In the work of Moldavskii and Nizovkina only 20–35% of the charge remained in the pentane fraction, the rest being converted to lighter and heavier fractions. The calculated values are therefore based on the equation

$$R \ln K_G{}^0 = (1861/T) - 1.299$$

which has been fitted only to the present results. The corresponding value of 1861 cal./mole for the heat of isomerization is in perfect agreement with the value of 1930 cal./mole given by Rossini.[8] The value of 1.30 e. u. for the entropy of isomerization is also in excellent agreement with the value of 1.12 e. u. based on third-law measurements of Messerly and Kennedy[18] for normal pentane and of Schumann, Aston and Sagenkahn[19] for isopentane.

TABLE X

ISOMERIZATION OF PENTANE

Observer	Temp., °C.	Obs. $K_G{}^0$	Obs. phase	% Isopentane in observed phase			
				Calcd.	Obs.		
This work	65	8.29	Liquid	87.2	86.5	87.9	
	150	4.76	Mixed	82.4	82.2	82.6	
	200	3.76	Vapor	79.0	77.3	79.0	80.7
Moldavskii	25	7.70	Liquid	90.4	85.7	85.8	
	50	5.55	Liquid	88.4	81.5	82.0	
	70	4.44	Liquid	86.8	77.7	79.5	
	90	3.32	Liquid	85.3	73.0	73.5	75.0
Schuit	80	5.37	Liquid	86.1	81.0	82.5	

It has been pointed out that all our measurements on pentane isomerization were made with hydrogen as a cracking suppressant, and that this may produce a dynamic steady state different from the true equilibrium. We are unable to give a scientifically rigorous answer to this criticism. Whenever practically irreversible side reactions are encountered, only these dynamic steady states can be measured. It is thermodynamically possible for a slow side reaction with a large free energy decrease to produce a shift from true equilibrium to steady state which is out of all proportion to the amount of the side reaction. For example, consider the reaction scheme

$$\begin{array}{rcll} A & \longrightarrow & B & k_1[A] \\ B & \longrightarrow & A & k_2[B] \\ (n+1)A & \longrightarrow & nB + C & k_3[A] \end{array}$$

where the third reaction represents an irreversible formation of *C* from *A*, coupled with the isomerization of *n* molecules of *A*, to give an over-all free energy decrease. This scheme gives a dynamic steady state

$$K_1{}^1 = \frac{[B]}{[A]} = \frac{k_1 + (n+f)k_3}{k_2}$$

where

$$0 < f < 1$$

The true equilibrium constant is of course

$$K_1 = \frac{[B]}{[A]} = \frac{k_1}{k_2}$$

The ratio is

$$\frac{K_1{}^1}{K_1} = 1 + (n+f)\frac{k_3}{k_1}$$

The free energy increase in converting *n* moles of A to B at steady state conditions is

$$nRT \ln \left[1 + (n+f)\frac{k_3}{k_1}\right]$$

The free energy decrease in converting one mole of A to C is *RT* ln *F*, where *F* is the ratio of the thermodynamic equilibrium concentration of C (with respect to A) to the actual concentration. The maximum possible value of *n* is then given by

$$\left[1 + (n+f)\frac{k_3}{k_1}\right]^n = F$$

When *F* is large and k_3/k_1 is small, values of *n* in the range 10–100 or even more are thermodynamically possible, and the steady state may be far from the true equilibrium. Almost all equilibrium measurements involving organic compounds are subject to this type of error. The efficient coupling of reactions assumed here, however, is virtually unknown in practice. When the amount of side reaction is large, it does not require such coupling to produce a seriously false steady state. It is considered a reasonable presumption, therefore, that the use of hydrogen, which greatly reduces side reaction, gives improved values for the pentane isomerization equilibrium.

Summary

1. The isomerization equilibria for butane and pentane have been studied under conditions of only slight side reactions.

2. The results for butane agree with previous equilibrium determinations, and may be represented by $R \ln K_G{}^0 = (2318/T) - 4.250$. The corresponding heat of reaction disagrees with the calorimetric value, but the entropy is in fair agreement with the third-law value.

3. The results for pentane disagree with the previous measurements, and lead to the equation $R \ln K_G{}^0 = (1861/T) - 1.299$. The indicated heat of reaction agrees exactly with the calorimetric value, and the agreement with the third-law entropy is very good.

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[18] G. H. Messerly and R. M. Kennedy, THIS JOURNAL, **62**, 2988 (1940).

[19] S. C. Schumann, J. G. Aston and M. Sagenkahn, *ibid.*, **64**, 1039 (1942).