

Equilibrium in the Gas Reaction, $\text{CHBr}_3 + \text{Br}_2 \rightleftharpoons \text{CHBr}_4 + \text{HBr}$

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found to be independent of the number of passages over the catalyst and the initial gas composition.*

A special analytical procedure was developed which enabled us to measure accurately the quantity of hydrogen and total olefine in the gas mixture, and also to determine the amount of ethylene or propylene in the olefinic fraction.

Applying the van't Hoff isochore to the data of Table I, the heats of the two reactions are calculated to be 34.0×10^3 calories per mole at 415°C , and 30.8×10^3 calories per mole

molecular models are used, even at high temperatures, provided the molecular constants are accurately known, as is the case for this reaction.

The good agreement of calculated and experimental equilibrium constants for the propane reaction is an additional strong evidence, if such be needed, that propylene has a potential barrier of about 2100 calories and not, as Pitzer claims,¹⁵ 800. Calculation of the equilibrium constant by Pitzer's assignment¹⁶ gives the value 10.0×10^{-4} at 375°C .

Detailed description of our work, as well as a discussion of the literature on the subject, will be published in this Journal with some delay because of pressure of national defense work.

TABLE I.

Temp.	Initial excess of:	Number of experiments	Equilibrium constant, atmos.	Average, atmos.
450°C	C ₂ H ₆	4	$5.12 \pm 0.09 \times 10^{-4}$	5.16×10^{-4}
	C ₂ H ₄ + H ₂	4	$5.21 \pm 0.04 \times 10^{-4}$	
380°C	C ₂ H ₆	3	$3.94 \pm 0.04 \times 10^{-5}$	4.04×10^{-5}
	C ₂ H ₄ + H ₂	3	$4.15 \pm 0.13 \times 10^{-5}$	
375°C	C ₃ H ₈	3	$5.25 \pm 0.08 \times 10^{-4}$	5.25×10^{-4}
	C ₃ H ₆ + H ₂	4	$5.26 \pm 0.01 \times 10^{-4}$	
310°C	C ₃ H ₈	1	3.69×10^{-5}	3.68×10^{-5}
	C ₃ H ₆ + H ₂	1	3.67×10^{-5}	

at 343°C . These values differ from those measured directly by Kistiakowsky *et al.*^{2,3} at 82°C and extrapolated to the higher temperatures by means of the available heat capacity data (33.9×10^3 and 31.1×10^3 , respectively) by only a few hundred calories, which can be caused by errors in the equilibrium constants of less than 2 percent. Errors of this magnitude we consider inherent in our measurements.

We have calculated statistically equilibrium constants for the ethane-ethylene-hydrogen system, using the heat of reaction as given in the reference above, and molecular constants as given by Stitt,⁴ Frost,⁵ Burcik, Eyster, and Yost,⁶ Smith,⁷ Giauque,⁸ and Davis and Johnston.⁹ The result is $K_p = 5.19 \times 10^{-4}$ at 450°C , for a potential barrier restricting internal rotation equal to 2750 calories per mole, as given by Kistiakowsky, Lacher, and Stitt.¹⁰ The equilibrium constant for the propane-propylene-hydrogen system has also been calculated statistically, using the heat of reaction as given by Kistiakowsky *et al.*³ The vibrational frequencies of propylene were taken from Wilson and Wells;¹¹ those of propane from Wu and Barker,¹² except that the four undetermined frequencies were taken as 2965, 1465, 1150, 1100. (This assignment gives heat capacities in satisfactory agreement with the experimental data reported by Kistiakowsky and Rice.¹³) Taking as the potential barriers restricting internal rotation 3300 calories for propane and 2100 for propylene, we obtain $K_p = 5.6 \times 10^{-4}$ at 375°C , using Pitzer's tables¹⁴ for the contributions from internal rotation.

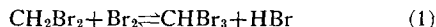
The excellent agreement of calculated and experimental equilibrium constants for the ethane reaction shows how trustworthy can be the statistical calculations although merely the simple rigid rotator and harmonic oscillator

- ¹ Frey and Huppke, *Ind. Eng. Chem.* **25**, 54 (1933).
² The slight effect of the initial gas composition on K evident from Table I is due to the inclusion in the averages of earlier runs made with an insufficiently aged catalyst.
³ Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.* **57**, 65 (1935).
⁴ Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.* **57**, 876 (1935).
⁵ F. Stitt, *J. Chem. Phys.* **7**, 297 (1939).
⁶ A. V. Frost, *Comptes rendus*, U. S. S. R. 161 (1933).
⁷ Burcik, Eyster, and Yost, *J. Chem. Phys.* **9**, 118 (1941).
⁸ L. G. Smith, *J. Chem. Phys.* **8**, 798 (1940).
⁹ W. F. Giauque, *J. Am. Chem. Soc.* **52**, 4816 (1930).
¹⁰ Davis and Johnston, *J. Am. Chem. Soc.* **56**, 1045 (1934).
¹¹ Kistiakowsky, Lacher, and Stitt, *J. Chem. Phys.* **7**, 289 (1939).
¹² E. B. Wilson, Jr. and A. J. Wells, *J. Chem. Phys.* **9**, 319 (1941).
¹³ V. L. Wu and E. F. Barker, *J. Chem. Phys.* **9**, 487 (1941).
¹⁴ G. B. Kistiakowsky and W. A. Rice, *J. Chem. Phys.* **8**, 610 (1940).
¹⁵ K. S. Pitzer, *J. Chem. Phys.* **5**, 469 (1937).
¹⁶ K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.* **9**, 485 (1941).
¹⁷ K. S. Pitzer, *J. Chem. Phys.* **5**, 473 (1937).

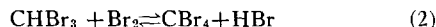
Equilibrium in the Gas Reaction, CHBr₃ + Br₂ ⇌ CBr₄ + HBr

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 December 11, 1941

RECENT calculations of partition functions for the bromomethanes¹ with other pertinent data indicate that such substitution reactions as



and



should be incomplete in the gas phase. This has been confirmed by preliminary determinations of equilibrium in the latter reaction.

Samples of liquid bromoform and bromine were weighed out in glass ampoules. These were introduced into a Pyrex tube which was then evacuated, sealed, and heated in a vapor bath (either naphthalene b.p. 218°C , or α -bromonaphthalene, b.p. 281°C). Total pressures in the reaction tubes at the operating temperatures were about 1 atmos.

After heating, the tubes were quenched in a water spray, opened under potassium iodide solution, and the solution titrated with thiosulphate and with alkali. Data on hydrogen bromide formed were usually a littler lower (1-3 percent) than for bromine reacting, indicating possible side reactions other than substitution. No appreciable amounts of permanent gas were detected.

Principal sources of uncertainty follow from the facts that equilibrium was only approached from the one side, and that no allowance could be made for the formation of lower bromides (especially methylene dibromide). However, it was shown that variation of the heating time (0.5 to 4 hours) indicated a quite definite end-point short of complete reaction. Further, by increasing the ratio of bromine to bromoform up to as much as 5 to 1, the formation of lower bromides could be minimized.

Results calculated for the equilibrium constant, $[CBr_4][HBr]/[CHBr_3][Br_2]$, gave values of 0.30 to 0.32 at 218°C, and 0.26 to 0.30 at 283°C, (six experiments each) with no definite trends.

An equilibrium constant was calculated from the statistical data at 500°K (227°C) for purposes of comparison. For the function, $(E_0 - F^0)/T$, Stevenson and Beach¹ find 73.56 and 78.43 at 500°K, for $CHBr_3$ and CBr_4 , respectively. Gordon and Barnes² find corresponding values for Br_2 and HBr to be 55.01 and 44.14, respectively. Thus, at 500°K $(\Delta E_0^0 - \Delta F^0)/T = -6.00$.

The value of ΔE_0^0 is uncertain. Judging from heats of formation at 18°C, as estimated by Bichowsky and Rossini,³ $\Delta E_{291}^0 = -2650$ cal. Calculated heat capacities indicate that this should be increased to about -3000 cal. at 0°K.

Substituting this value for ΔE_0^0 , one obtains $\Delta F_{500}^0 = 0$, when $K_{500} = 1$, which is in fair agreement with the experimental data in the corresponding temperature range. A value of ΔE_0^0 nearer -1800 cal. would yield better agreement, and would be in better accord with the small observed temperature coefficient of the equilibrium constant.

To this extent, the calculations of Stevenson and Beach are confirmed.

¹ D. P. Stevenson and J. Y. Beach, *J. Chem. Phys.* **6**, 25, 341 (1938).

² Gordon and Barnes, *J. Chem. Phys.* **1**, 692 (1933).

³ Bichowsky and Rossini, *Thermochemistry* (Reinhold Publishing Company, New York, 1936).

Erratum: The Partition Function of Molecules with Internal Torsion

I. Single Asymmetric Top Attached to Rigid Framework

[*J. Chem. Phys.* **9**, 807-815 (1941)]

DONNA PRICE

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Page (subscript gives column)	Line	Corrected form
810 ₁	Fine print, sixth equation.	$\eta^2 = C^2 + E^2 - 2\Sigma\alpha\alpha'\alpha''\alpha'''EC = E^2 + C^2$
810 ₁	Fine print, two lines above (14)	$\Sigma\alpha\alpha'\alpha''\alpha''' \leq 0.058; \lambda^2 M^{-1} = 0.013$
810 ₂	1	(13) instead of (14).
812 ₁	4 and 6	h inserted before $\sqrt{2}$.
812 ₁	12	$a_{30}C$ divided by qa .
812 ₁	Eqs. (29) and (30)	R^2, I^2, S^2 instead of R^2, I^2, S^2 .
812 ₁	Eq. (29), last term	3 instead of 5.
812 ₁	Third line below (30)	$S = C\Sigma\alpha\alpha'\alpha''\alpha'''P_{\alpha}$.
812 ₂	Eq. (33), line 1	D_0 instead of D_1 .
813 ₁	2	D_0 instead of D_1 .
813 ₂	3	$\sigma = AC^2\Sigma\alpha\alpha'\alpha''\alpha'''$.
814 ₂	8	+ precedes sum.

The last part of footnote 12, p. 814, should read: $M_{\pm 1}$ and $M_{\pm 2}$ are the same as above except for the factors of $\frac{1}{2}$ and $\frac{1}{4}$, respectively, instead of $\frac{1}{2}$.

$$N_{ij} = \delta_{ij} \square_i - A \Delta_i \Delta_j Y_{ij},$$

$$Y_{ij} = \begin{cases} [g_i g_j Y + \frac{1}{2} \beta^{-1} f_i f_j], & i, j \leq 3 \\ [q_i q_j Y + L(q_i a_{3j} + q_j a_{3i}) + C^2 a_{3i} a_{3j} + \frac{1}{2} \beta^{-1} l_i l_j], & i, j > 3 \\ [g_i q_j Y + L g_i a_{3j} + \frac{1}{2} \beta^{-1} f_i l_j], & i \leq 3, j > 3 \end{cases}$$

where $Y = (1 - \frac{1}{2} \beta^{-1} + \frac{3}{16} \beta^{-2})$, and $L = C(1 - \frac{1}{4} \beta^{-1})$.

$$E_{ij} = -\Delta_i \Delta_j M \begin{cases} [g_i g_j E + \beta^{-1} f_i f_j], & i, j \leq 3 \\ [q_i q_j E - \frac{1}{2} \beta^{-1} (q_i a_{3j} + q_j a_{3i}) C + \beta^{-1} l_i l_j], & i, j > 3 \\ [g_i q_j E - \frac{1}{2} \beta^{-1} g_i a_{3j} C + \beta^{-1} f_i l_j], & i \leq 3, j > 3 \end{cases}$$

where $E = (\frac{3}{8} \beta^{-2} - \beta^{-1})$. F_{ij} should also include the factor A as does E_{ij} .