

The Limiting High Temperature Rotational Partition Function of Nonrigid Molecules VI. The Methanol Equilibrium

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Citation: [The Journal of Chemical Physics](#) **4**, 493 (1936); doi: 10.1063/1.1749890

View online: <http://dx.doi.org/10.1063/1.1749890>

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J. Chem. Phys. **4**, 276 (1936); 10.1063/1.1749835



plate voltage are sufficiently linear to permit extrapolation and determination of the constants of the diode.

DISCUSSION OF RESULTS

It is seen that the value found for the electron affinity of bromine atoms in the present experiments agrees with the only other *direct* experimental determination of Piccardi.³ However it was hoped that the indirectly found value of Mayer and Helmholtz² could be checked, because they obtained their result from several bromides. It is conceivable that the bromine used by us was not of sufficient purity. The experiments reported here will be repeated at some future time and it is hoped that by using further extraordinary precautions it will be possible to give a definite answer. Since it is impossible to tell at the moment when this research can be continued, it was thought proper to report the present findings.

We are indebted to the research grant committee of the Graduate School of the University of Minnesota for financial assistance which enabled us to carry out this investigation.

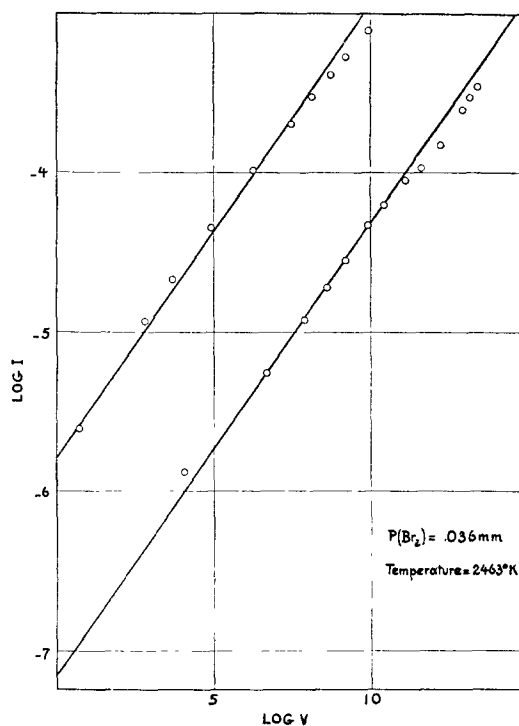


FIG. 1. Current-potential curve in vacuum and in bromine gas.

The Limiting High Temperature Rotational Partition Function of Nonrigid Molecules

VI. The Methanol Equilibrium¹

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(Received May 23, 1936)

The entropy of methanol and the equilibrium constant for methanol synthesis are calculated for two molecular models, one of which rotates freely about the CO bond, while the other possesses a torsional oscillation of frequency 700 cm^{-1} about that bond. The latter model is indicated by spectroscopic evidence and gives an entropy in close agreement with the third law value and an equilibrium constant close to the mean of the widely scattered

experimental results. The former model is supported strongly by valence theory; it can be made to agree with the third law entropy by assuming a zero-point entropy of $R \log 3$, and its rather poor agreement with experimental equilibrium data is not conclusive evidence against it. The true equilibrium constant probably lies between these two calculated values, or at worst slightly beyond one of them.

THE equilibrium constant for the reaction

$$2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}$$

has been determined many times. The extreme

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values at a single temperature are in some cases in the ratio of eight to one, and there is little reason to have confidence in the average values. This is particularly so because of the occurrence of undesired side reactions. It is

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therefore of considerable interest to determine whether a more accurate value can be calculated from spectroscopic data.

Unfortunately neither the configuration nor the vibration frequencies of methanol are completely known. Pauling and Brockway³ found from electron-diffraction measurements with methyl ether a CO distance of 1.42×10^{-8} cm and a COC angle of 111° . Reasonable values for the water molecule, based on spectroscopic data, are 0.95×10^{-8} cm for the OH distance and 105° for the HOH angle. The value of 110° for the COH angle is used in the following calculations, together with distances $d_{CO} = 1.42 \times 10^{-8}$ cm, $d_{OH} = 0.95 \times 10^{-8}$ cm, $d_{CH} = 1.11 \times 10^{-8}$ cm. The carbon valences are assumed to be at exact tetrahedral angles. It is then easy to calculate, using methods which have previously been developed,⁴ that if there is free rotation about the CO bond the translation-rotation entropy is

$$S_{t+r} = 6.375 + (9/2)R \log T, \\ S_{t+r, 298} = 57.316,$$

while if this rotation is completely inhibited, the entropy is

$$S_{t+r} = 10.089 + 4R \log T, \\ S_{t+r, 298} = 55.370.$$

The most complete analysis of the vibration spectrum is that of Bartholomé and Sachsse,⁵ who give

$\nu(\pi)_{CH}$	2943–2835 cm^{-1}	(resonance with $2^2\delta(\sigma)_{CH}$)
$2\nu(\sigma)_{CH}$	3000	
$\delta(\pi)_{CH}$	1360	
$2^2\delta(\sigma)_{CH}$	1470	
ν_{OH}	3400	
ν_{CH_3-OH}	1025	
³ or ⁴ δ_{CH_3-OH}	690, 725, —, —.	

The δ_{CH_3-OH} vibration will be triple if there is free rotation, quadruple if the rotation is frozen. Bartholomé and Sachsse consider that the appearance of the spectrum favors the latter alternative. They propose 700 cm^{-1} as a probable value for both unobserved δ_{CH_3-OH} frequencies. One of these frequencies corresponds to torsion

about the CO bond, however, and in order to have a torsion frequency of this magnitude, it is necessary for the potential energy barrier opposing free rotation to be at least 3000 cal. For the somewhat similar case of ethane, Eucken and Weigert⁶ calculated from low-temperature specific-heat measurements a potential barrier of 315 cal., and Eyring⁷ estimated 350 cal. from valence theory. A calculation similar to Eyring's gave 300 cal. for the potential barrier in methanol. This value might be somewhat increased by the effect of the OH dipole moment, but it scarcely seems possible to account for a value of 3000 cal. in that way. In view of this difficulty in understanding such a high torsion frequency, calculations will be made for two cases: (a) free rotation and three δ_{CH_3-OH} frequencies at 700 cm^{-1} ; (b) inhibited rotation and four δ_{CH_3-OH} frequencies at 700 cm^{-1} .

For the hypothetical perfect gas at atmospheric pressure, with free rotation $S_{298} = 58.38$ and without free rotation $S_{298} = 56.74$. The third-law value found by Kelley⁸ for the liquid is $S_{298} = 30.26 \pm 0.2$. From this value, the vapor pressure,⁹ and the very accurate heat of vaporization determined by Fiock, Ginnings and Holton,¹⁰ the value for the gas is $S_{298} = 56.63$. The third-law entropy is based on specific-heat measurements down to 16.5°K , and Kelley's estimate of error for it seems reliable. The calculation of ΔS_{vap} should be correct to within 0.05 e.u. If the COH angle were 115° instead of 110° , the entropy of the freely rotating molecule would be reduced by 0.07 e.u. A uniform decrease of all bond distances by five percent would reduce the entropy by 0.39 e.u. The total vibrational contribution of 1.06 e.u. depends to the extent of 0.75 e.u. on directly observed frequencies, hence is certainly not more than 0.31 e.u. too high. The cumulative effect of all these very liberal estimates reduces the disagreement between the third-law result and the calculated value for free rotation from 1.75 e.u. to 0.73 e.u. This is still markedly unsatisfactory. The third-law result,

⁶ Eucken and Weigert, *Zeits. f. physik. Chemie* **B23**, 265 (1933).

⁷ Eyring, *J. Am. Chem. Soc.* **54**, 3191 (1932).

⁸ Kelley, *J. Am. Chem. Soc.* **51**, 181 (1929).

⁹ *International Critical Tables*, vol. 3, p. 216.

¹⁰ Fiock, Ginnings and Holton, *Bur. Standards J. Research* **6**, 881 (1931).

³ Pauling and Brockway, *J. Am. Chem. Soc.* **57**, 2684 (1935).

⁴ Kassel, *J. Chem. Phys.* **4**, 276 (1936).

⁵ Bartholomé and Sachsse, *Zeits. f. physik. Chemie* **B30**, 40 (1935).

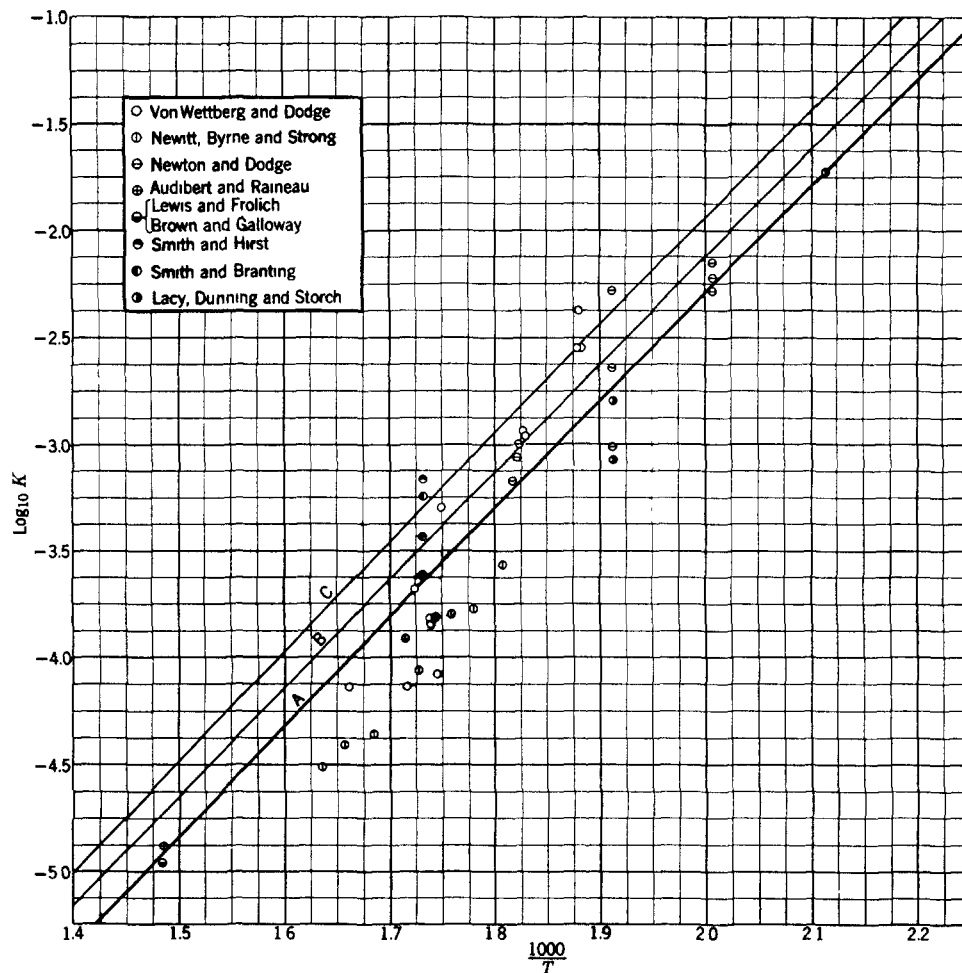


FIG. 1. Equilibrium constants for methanol synthesis.

however, can be reconciled with free rotation about the CO bond by assuming that because of lack of order in the actual crystal there is an unmeasured entropy of $R \log 3$ or slightly less. The corrected third-law value is then 58.81 e.u., or somewhat less than this value if there is partial ordering; the agreement with the theoretical value of 58.38 e.u. is sufficiently good. The very good direct agreement of the third-law value with the calculation based on lack of free rotation is to some extent fortuitous, since the estimate of 700 cm^{-1} for the two unobserved frequencies may well have introduced an error of several tenths of an entropy unit. This agreement, nevertheless, certainly provides evidence in favor of torsion rather than free rotation about the CO bond.

Since it is hard to understand the existence of a potential barrier high enough to permit even one excited state of CO torsion, it is probable that higher states will be rotational. Lack of knowledge as to these higher states limits the temperature range within which reasonably accurate calculations for the torsion model can be made. At 750°K , however, where $-F/T$ for a harmonic oscillator with frequency 700 cm^{-1} is 0.606, $-F/T$ for a system with only one excited level 700 cm^{-1} above the normal is 0.464. The position and character of the higher levels thus cannot make any great difference up to this temperature.

Table I gives $-(F^\circ - E_0^\circ)/T$ for methanol and $\log_{10} K$ for $2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}$ up to 750°K for both torsion and free rotation models. In making

TABLE I. "Free energy" and equilibrium constant for methanol.

$T, ^\circ\text{K}$	TORSION		FREE ROTATION	
	$-(F^\circ - E_0^\circ)/T$	$\log_{10} K$	$-(F^\circ - E_0^\circ)/T$	$\log_{10} K$
298.1	47.716	4.322	48.602	4.680
300	47.774	4.221	48.663	4.578
350	49.208	1.939	50.205	2.297
400	50.518	.199	51.594	.557
450	51.738	-1.175	52.874	-.818
500	52.884	-2.288	54.064	-1.932
550	53.975	-3.207	55.186	-2.853
600	55.012	-3.980	56.246	-3.629
650	56.009	-4.638	57.258	-4.290
700	56.962	-5.207	58.220	-4.862
750	57.875	-5.703	59.139	-5.361

these calculations, $-F/T$ for hydrogen has been taken from the tabulation of Giauque,¹¹ and H from that of Davis and Johnston.¹² For carbon monoxide the revised $-F/T$ values of Clayton and Giauque¹³ are used, and H is taken from the work of Johnston and Davis.¹⁴ Rossini's accurate values are used for the heats of combustion of hydrogen,¹⁵ carbon monoxide,¹⁶ and gaseous methyl alcohol.¹⁷ Curve *A* in Fig. 1 reproduces the equilibrium constants calculated for the torsion model, and curve *C* those for free rotation. The points represent experimental results of Lewis and Frolich,¹⁸ Brown and Galloway,¹⁹ Audibert and Raineau,²⁰ Smith and Branting,²¹ Newitt, Byrne and Strong,²² Lacy,

Dunning and Storch,²³ Smith and Hirst,²⁴ von Wettberg and Dodge²⁵ and Newton and Dodge,²⁶ all corrected to zero pressure by Newton and Dodge.

The agreement of curve *C* with the experimental results can scarcely be considered good, but it would require considerable courage to reject the assumption of free rotation on that basis alone.

Curve *B* is included to show the effect of shifting the two unobserved frequencies for the torsion model from 700 cm^{-1} to 500 cm^{-1} . The displacement of the equilibrium constant is relatively unimportant, but the calculated entropy becomes $S_{298} = 57.45$, in rather definite disagreement with experiment.

It does not appear possible at present to reach any final decision with regard to rotation about the CO bond. Evidence in favor of a torsional oscillation about this bond is provided by the absorption spectrum, the entropy, and rather feebly by the equilibrium constant. Valence theory, however, seems to demand free, or very nearly free, rotation about this bond; this model can be harmonized with third-law results by assuming a zero-point entropy of $R \log 3$, and is not entirely incompatible with equilibrium data. Aside from the uncertainty about this one point, there does not seem to be much possibility of any considerable error in the calculations. The true equilibrium constant, therefore, should lie between curves *A* and *C*, or at worst slightly outside those limits.

¹¹ Giauque, J. Am. Chem. Soc. **52**, 4816 (1930).

¹² Davis and Johnston, J. Am. Chem. Soc. **56**, 1045 (1934).

¹³ Clayton and Giauque, J. Am. Chem. Soc. **55**, 5071 (1933).

¹⁴ Johnston and Davis, J. Am. Chem. Soc. **56**, 271 (1934).

¹⁵ Rossini, Bur. Standards J. Research **6**, 1 (1931).

¹⁶ Rossini, Bur. Standards J. Research **6**, 37 (1931).

¹⁷ Rossini, Bur. Standards J. Research **8**, 119 (1932).

¹⁸ Lewis and Frolich, Ind. Eng. Chem. **20**, 285 (1928).

¹⁹ Brown and Galloway, Ind. Eng. Chem. **20**, 960 (1928).

²⁰ Audibert and Raineau, Ind. Eng. Chem. **20**, 1105 (1928).

²¹ Smith and Branting, J. Am. Chem. Soc. **51**, 129 (1929).

²² Newitt, Byrne and Strong, Proc. Roy. Soc. **A123**, 236 (1929).

²³ Lacy, Dunning and Storch, J. Am. Chem. Soc. **52**, 926 (1930).

²⁴ Smith and Hirst, Ind. Eng. Chem. **22**, 1037 (1930).

²⁵ von Wettberg and Dodge, Ind. Eng. Chem. **22**, 1040 (1930).

²⁶ Newton and Dodge, J. Am. Chem. Soc. **56**, 1287 (1934).