Closure, Resonance, Bond and Activation Entropy

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(Received December 20, 1951)

Introduction

According to Sackur-Lewis(1) the molecular entropy of the monoatomic gas molecule is given theoretically by the equation:

$$S=5/2\cdot R\ln T-R\ln P+3/2\cdot R\ln M-2.63, \tag{1}$$

where R is universal gas constant, and M is molecular weight. At the state of 298.2°K and 1 atm. eq. (1) becomes

$$S^\circ=26+3/2\cdot R\ln M, \tag{2}$$

where S° is molecular entropy at 298.2°K and 1 atm. As to diatomic molecule Eastman,(2) for example, has given the empirical rule:

$$S^\circ=29+3/2\cdot R\ln(XY)+0.7\ln M. \tag{3}$$

Because of difficulty of expressing the molecular entropy of polyatomic gas molecule by means of a simple equation, the empirical treatment of this entropy has been performed chiefly from the standpoint of atomic group regularity. Parks-Huffman(3) have, for example, systematized the entropy change assigned to the displacement of atomic groups, and Bremner-Thomas(4) have constructed the atomic group equation. The empirical rules of simple form such as Wenner's(5)

$$\log S^\circ=A\log M+\log B \tag{4}$$

and Kobozev's(6)

$$S^\circ=26+3\ln M+1.45\times M^{3/4} \tag{5}$$

are not so accurate for practical use.

From the standpoint of chemical bond we have constructed a new empirical rule for the calculation of molecular entropy of general gas molecule, which has sufficient accuracy and wide range of application, and have discussed the relations of entropy to the molecular structure and the frequency factor of chemical reaction quantitatively.

Empirical Rule

The empirical rule is expressed by the equation:

$$S^\circ=26+3/2\cdot R\ln\overset{n}{\Pi}(X)+0.7\ln\overset{m}{\Pi}\left(\frac{X+Y}{e^{\alpha}}\right), \tag{6}$$

where S° is molecular entropy of ideal gas at 298.2°K and 1 atm., R is universal gas constant, i. e., 1.987 cal·degree^{-1}, X is atomic weight, n is number of atoms in the molecule, $X+Y$ is sum of atomic weights of atoms joined with the bond, m is total number of bonds in the molecule, and finally α is a parameter given by the equation:

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(1) O. Sackur, *Ann. Phys.*, **36**, 958 (1911); G. N. Lewis, *Phys. Rev.*, **18**, 121 (1921).

(2) E. D. Eastman, *J. Am. Chem. Soc.*, **45**, 80 (1923).

(3) G. S. Parks and H. M. Huffman, "The Free Energy of Some Organic Compounds", New York, 1932.

(4) J. G. M. Bremner and G. D. Thomas, *Trans, Faraday Soc.*, **43**, 779 (1947).

(5) R. P. Wenner, *Chem. Eng. Progress*, **45**, 194 (1949).

(6) N. I. Kobozev, *Zhur. Fiz. Khim.*, **22**, 1002 (1948).

$$\alpha = 9^{3-n} - \frac{15.7}{m} + 1.9^{N} + \frac{B^2}{1.8} + 5/4 \cdot n_X - f. \qquad (7)$$

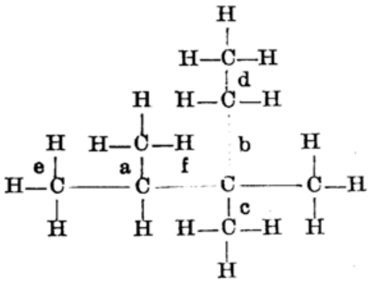
The third term of eq. (6), which has been derived from the standpoint of chemical bond, is the principal feature of the rule, where m is expressed generally with

$$m = n - 1, \qquad (8)$$

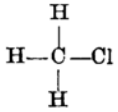
but for the compound of ring structure with

$$m = n,\ n+1,\ \cdots\cdots. \qquad (9)$$

In eq. (7) N is bond order, and so $N=1$ for single bond and $N=3$ for triple bond, but must be taken $N=1$ for double bond and for bond in diatomic molecule. B is the degree of branching of the bond, which is counted as follows:



(A)



H_3C-Cl

(B)

H—C≡C—H

(C)

H—Cl

(D)

In molecule (A) $B=2$ for bond a, $B=3$ for bonds b and c, and $B=0$ for all other bonds d, e, f, etc. In molecules (B), (C), and (D), namely in the molecules, which are constructed with the central atom or central atomic pair joined with multiple bond, and surrounding atoms, $B=-1$ for all bonds concerned. In diatomic molecule, therefore, $B=-1$ always.

The fifth term of eq. (7) is the correction term for the bond involving the seventh group non-metallic element, i. e., halogen, where n_X is number of halogen atoms joined to the same atom, but must be taken as zero in diatomic molecule. The sixth term f of eq. (7) is the correction term for the bond involving the fifth and sixth group non-metallic element, and is counted as follows:

$f=3$ (for the single bond joining the central atom and the atomic group, when the molecule is constructed with the central 5th or 6th group atom and surrounding one atomic group and several atoms),

$f=2$ (for the single bond between 5th or 6th group atoms each other),

$f=0$ (for all other bonds).

For example,

$f=3$ (for C—N of amine, C—O of alcohol, C—S of mercaptane),

$f=2$ (for N—N, O—O, S—S, N—O),

and for diatomic molecule $f=0$ inevitably.

Simpler Method of Calculation

In special cases as below the rule becomes simpler. For monoatomic molecule, for example, the bond term of eq. (6) disappears, and so the rule is reduced to

$$S^\circ = 26 + 3/2 \cdot R \ln X, \qquad (10)$$

which agrees with the equation of Sackur-Lewis.

For diatomic molecule $n=2$, $m=1$, $N=1$, $B=-1$, $n_X=0$, and $f=0$, so that the rule becomes

$$\begin{aligned} S^\circ &= 26 + 3/2 \cdot R \ln (XY) + 0.7 \ln (X+Y) \\ &\quad - 0.7 \times \{9 - 15.7 + 1.9 + 0.55\} \\ &= 29 + 3/2 \cdot R \ln (XY) + 0.7 \ln (X+Y), \qquad (11) \end{aligned}$$

which agrees with the equation of Eastman.

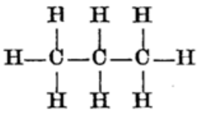
For non-branched hydrocarbons involving more than two carbon atoms, excluding ethylene and acetylene, $n \geqq 5$, $B=0$, $n_X=0$, and $f=0$, and so the rule becomes

$$\begin{aligned} S^\circ &= 26 + 3/2 \cdot R \ln \overset{n}{\Pi} (X) + 0.7 \ln \overset{m}{\Pi} (X+Y) \\ &\quad - 0.7 \times \overset{m}{\Sigma} \left\{ -\frac{15.7}{m} + 1.9^{N} \right\} \\ &= 37 + 3/2 \cdot R \ln \overset{n}{\Pi} (X) + 0.7 \ln \overset{m}{\Pi} (X+Y) \\ &\quad - 0.7 \times \overset{m}{\Sigma} 1.9^{N}. \qquad (12) \end{aligned}$$

Finally for non-branched saturated hydrocarbons or non-branched olefines involving more than two carbon atoms, excluding ethylene, $n \geqq 5$, $B=0$, $n_X=0$, $f=0$, and $N=1$, and so the rule becomes from eq. (12)

$$\begin{aligned} S^\circ &= 37 + 3/2 \cdot R \ln \overset{n}{\Pi} (X) + 0.7 \ln \overset{m}{\Pi} (X+Y) \\ &\quad - 1.33\, m. \qquad (13) \end{aligned}$$

As a typical example S° of propane (C_3H_8) is calculated



$H_3C-CH_2-CH_3$

from eq. (13) as follows:

$$\begin{aligned} S^\circ &= 37 + 2.98 \times 3 \ln 12 + 0.7 \times \{8 \ln 13 + 2 \ln 24\} \\ &\quad - 1.33 \times 10 \\ &= 37 + 22.2 + 18.8 - 13.3 = 64.7 \text{ (e.u.)}, \end{aligned}$$

while the observed value of S° is 64.5 e.u.

Application of Empirical Rule

In Table 1 the calculated values of molecular

Table 1

Application of Empirical Rule

(unit e. u.; * exceptions)

Substance		$S^\circ_{\text{calc.}}$	$S^\circ_{\text{obs.}}$	Δ
H	Hydrogen atom	26.0	25.7	0.3
Cl	Chlorine atom	36.7	36.9	−0.2
Br	Bromine atom	39.1	38.8	0.3
I	Iodine atom	40.6	40.2	0.4
He	Helium atom	30.2	29.2	1.0
A	Argon atom	37.0	36.4	0.6
Cd	Cadmium atom	40.2	40.0	0.2
Hg	Mercury atom	41.9	41.5	0.4
Ca	Calcium atom	37.1	36.7	0.4
K	Potassium atom	37.0	36.6	0.4
Li	Lithium atom	31.8	31.5	0.3
P	Phosphorus atom	36.3	36.0	0.3
Rb	Rubidium atom	39.3	39.0	0.3
S	Sulphur atom	36.4	36.0	0.4
Cs	Caesium atom	40.7	40.3	0.4
Na	Sodium atom	35.4	35.1	0.3
Zn	Zinc atom	38.5	38.2	0.3
H_2	Hydrogen	29.5	31.2	−1.7
F_2	Fluorine	49.1	48.6	0.5
Cl_2	Chlorine	53.2	53.3	−0.1
Br_2	Bromine	58.7	59.1	−0.4
I_2	Iodine	61.9	61.8	0.1
HCl	Hydrogen chloride	42.2	43.3	1.1
HBr	Hydrogen bromide	45.2	47.0	−1.8
HI	Hydrogen iodide	47.0	47.5	−0.5
TlCl	Talium chloride	59.3	59.1	0.2
TlBr	Talium bromide	61.9	61.7	0.2
TlI	Talium iodide	63.5	63.6	−0.1
AgCl	Silver chloride	57.3	56.5	0.8
NaCl	Sodium chloride	51.9	52.9	−1.0
KCl	Potassium chloride	53.5	55.2	−1.7
H_2O	Water	44.4	45.1	−0.7
H_2S	Hydrogen sulphide	47.4	48.2	−0.8
NH_3	Ammonia	45.3	45.9	−0.6
PH_3	Phosphine	49.3	50.2	−0.9
PCl_3	Phosphorus trichloride	74.8	74.5	0.3
PBr_3	Phosphorus tribromide	83.2	83.1	0.1
CH_4	Methane	44.9	44.5	0.4
C_2H_6	Ethane	55.5	54.9	0.6
C_2H_5Cl	Ethyl chloride	66.1	65.9	0.2
$CH_2Cl \cdot CH_2Cl$	1, 2-dichloroethane	76.8	78.2	−1.4
$(CH_3)_2S$	Dimethyl sulphide	67.6	68.3	−0.7
CH_3OH	Methanol	57.8	57.7	0.1
C_2H_5OH	Ethanol	67.2	67.3	−0.1
CH_3SH	Methyl mercaptane	60.7	60.9	−0.2
C_2H_5SH	Ethyl mercaptane	70.1	70.6	−0.5
CH_3NH_2	Methyl amine	57.8	57.7	0.1
$(CH_3)_2NH$	Dimethyl amine	64.8	65.2	−0.4
CH_3F	Methyl fluoride	53.4	53.3	0.1
CH_3Cl	Methyl chloride	55.4	56.0	−0.6
CH_3Br	Methyl bromide	58.4	58.7	−0.3
CH_3I	Methyl iodide	60.2	60.9	−0.7
CH_2Cl_2	Dichloromethane	64.4	64.7	−0.3
CH_2Br_2	Dibromomethane	70.1	70.8	−0.7
$CHCl_3$	Chloroform	71.7	70.8	0.9
$CHBr_3$	Bromoform	80.1	79.1	1.0
PCl_5	Phosphorus pentachloride	84.9	84.3	0.6
CH_3CHO	Acetaldehyde	63.8	63.2	0.6
CH_3OCH_3	Dimethyl ether	65.0	65.6	−0.6
CH_3CN	Methyl cyanide	59.5	58.2	1.3
$(CH_3)_2S_2$	2, 3-Dithiabutane	80.9	80.5	0.4
N_2H_4	Hydrazine	57.4	57.0	0.4
CH_3NHNH_2	Methyl hydrazine	66.6	66.6	0
C_3H_8	Propane	64.7	64.5	0.2
n-C_4H_{10}	n-Butane	73.8	74.1	−0.3
n-C_5H_{12}	n-Pentane	83.0	83.3	−0.3
n-C_6H_{14}	n-Hexane	92.2	92.5	−0.3
n-C_7H_{16}	n-Heptane	101.4	101.6	−0.2
n-C_8H_{18}	n-Octane	110.6	110.8	−0.2
n-C_9H_{20}	n-Nonane	119.8	120.0	−0.2
n-$C_{10}H_{22}$	n-Decane	129.0	129.2	−0.2
n-$C_{11}H_{24}$	n-Undecane	138.2	138.4	−0.2
n-$C_{12}H_{26}$	n-Dodecane	147.4	147.6	−0.2
n-$C_{13}H_{28}$	n-Tridecane	156.6	156.7	−0.1
n-$C_{14}H_{30}$	n-Tetradecane	165.8	165.7	0.1
n-$C_{15}H_{32}$	n-Pentadecane	175.0	175.1	−0.1
n-$C_{16}H_{34}$	n-Hexadecane	184.2	184.3	−0.1
n-$C_{17}H_{36}$	n-Heptadecane	193.4	193.5	−0.1
n-$C_{18}H_{38}$	n-Octadecane	202.6	202.7	−0.1
n-$C_{19}H_{40}$	n-Nonadecane	211.8	211.8	0
n-$C_{20}H_{42}$	n-Eicosane	221.0	221.0	0
C_4H_{10}	2-Methyl propane (Isobutane)	72.0	71.3	0.7
C_5H_{12}	2-Methyl butane (Isopentane)	81.4	82.0	−0.6
$C(CH_3)_4$	2, 2-Dimethyl propane (Neopentane)	76.0	76.9	−0.9
$Si(CH_3)_4$	Silicon tetramethyl	80.4	85.8	−5.4*
C_6H_{14}	2-Methyl pentane	90.6	90.7	−0.1
〃	3-Methyl pentane	90.6	90.8	−0.2
〃	2,2-Dimethyl butane	85.2	85.7	−0.5
〃	2,3-Dimethyl butane	89.0	87.3	1.7
C_7H_{16}	2-Methyl hexane	99.8	99.6	0.2
〃	3-Methyl hexane	99.8	101.4	−1.6
〃	3-Ethyl pentane	99.8	98.5	1.3
〃	2, 2-Dimethyl pentane	94.4	93.6	0.8
〃	2, 3-Dimethyl pentane	98.2	99.0	−0.8
〃	2, 4-Dimethyl pentane	98.2	94.8	3.4*
〃	3, 3-Dimethyl pentane	94.4	95.5	−1.1
〃	2, 2, 3-Trimethyl butane	92.8	92.5	0.3
C_8H_{18}	2-Methyl heptane	109.0	108.8	0.2
〃	3-Methyl heptane	109.0	110.3	−1.3
〃	4-Methyl heptane	109.0	108.4	0.6
〃	3-Ethyl hexane	109.0	109.5	−0.5

Substance		$S°_{calc.}$	$S°_{obs.}$	Δ
C_8H_{18}	2, 2-Dimethyl hexane	101.6	103.1	−1.5
〃	2, 3-Dimethyl hexane	105.4	106.1	−0.7
〃	2, 4-Dimethyl hexane	105.4	106.5	−1.1
〃	2, 5-Dimethyl hexane	105.4	104.9	0.5
〃	3, 3-Dimethyl hexane	101.6	104.7	−3.1*
〃	3, 4-Dimethyl hexane	105.4	104.3	1.1
〃	2-Methyl-3-ethyl pentane	105.4	105.4	0
〃	3-Methyl-3-ethyl pentane	101.6	103.5	−1.9
〃	2, 2, 3-Trimethyl pentane	100.0	101.6	−1.6
〃	2, 2, 4-Trimethyl pentane	100.0	101.6	−1.6
〃	2, 3, 3-Trimethyl pentane	100.0	103.1	−3.1*
〃	2, 3, 4-Trimethyl pentane	103.8	103.0	0.8
〃	2, 2, 3, 3-Tetra-methyl butane	94.6	94.3	0.3
C_2H_4	Ethene (Ethylene)	52.7	52.5	0.2
C_3H_6	Propene (propylene)	63.6	63.8	−0.2
C_4H_8	1-Butene	73.1	73.5	−0.4
〃	2-Butene (cis and trans)	73.1	71.4 (mean)	1.7
〃	2-Methyl-2-propene	71.5	70.2	1.3
C_5H_{10}	1-Pentene	82.3	83.1	−0.8
〃	2-Pentene (cis and trans)	82.3	82.3 (mean)	0
C_5H_{10}	2-Methyl-1-butene	80.7	81.7	−1.0
〃	3-Methyl-1-butene	80.7	79.7	1.0
〃	2-Methyl-2-butene	80.7	80.9	−0.2
C_6H_{12}	1-Hexene	91.5	92.3	−0.8
〃	2-Hexene (cis and trans)	91.5	91.9 (mean)	−0.4
C_2H_2	Ethyne (Acetylene)	48.8	48.0	0.8
C_3H_4	Propyne (Methyl acetylene	59.3	59.3	0
C_4H_6	1-Butyne	68.5	69.5	−1.0
〃	2-Butyne	68.5	67.7	0.8
C_5H_8	1-Pentyne	77.7	79.1	−1.4
〃	2-Pentyne	77.7	79.3	−1.6
〃	3-Methyl-1-butyne	76.2	76.2	0
〃	1, 4-Pentadiene	81.2	79.7	1,5
C_5H_{10}	Trimethylethylene	80.8	79.7	1.1
O_2	Oxygen	48.0	48.0	0
S_2	Sulphur	52.6	53.5	−0.9
N_2	Nitrogen	47.0	45.6	1.4
P_2	Phosphorus	52.4	52.2	0.2
PN	Phosphorus nitride	49.8	50.4	−0.6

entropies of various molecules by means of this rule were compared with the observed values,(7) i. e., the thermal entropies calculated thermodynamically from the calorimetric data, using the third law, or the statistical entropies calculated statistically from the spectroscopic data, excluding the weight of nuclear spin. The error of the observed value is sometimes ±1 e.u., and in special cases often ±2 e.u. absolutely.

In 140 instances shown in Table 1 the present rule is applicable for 136 instances within the error of ±2 e. u., and for 112 instances within the error of ±1 e.u. But in the present rule the difference between the isomers, excluding branched isomers, i.e., *D-L*, cis-trans, *o-m-p*, etc., are not involved. These effects are, however, not so large that they are included within the error of the rule. For the compounds of ring structure and those having resonance effect the present rule is not applicable. The discrepancies in such cases are rather suitable quantities in discussing the relation between entropy and molecular structure as will be stated below.

Abnormal Depression of Entropy

Abnormal depression of entropy, which is defined as the positive difference between the calculated entropy by means of the present rule and the observed entropy, can be interpreted with the depression due to ring closure, *Closure entropy*, and the depression due to resonance effect, *Resonance entropy*.

The values of closure entropies of some substances are tabulated in Table 2. For the ring of 3, 5 and 6 members the closure entropies are about 7, 13 and 18 e.u. respectively. The closure entropy 20.9 e.u. of cyclohexane agrees well with

Table 2

Closure Entropy (unit, e. u.)

Substance		No. of memb. of ring	$S°_{calc.}$	$S°_{obs.}$	Closure entropy
C_3H_6	Cyclopropane	3	64.6	56.8	7.8
O_3	Ozone	3	62.8	57.0	5.8
C_2H_4O	Ethylene oxide	3	64.7	57.9	6.8
C_5H_{10}	Cyclopentane	5	83.3	70.7	12.6
C_6H_{12}	Cyclohexane	6	92.2	71.3	20.9
C_7H_{14}	Methyl cyclohexane	6	99.8	82.1	17.7
C_8H_{16}	Ethyl cyclohexane	6	109.0	91.5	17.5
C_8H_{16}	1, 1-Dimethyl cyclohexane	6	103.6	87.2	16.4
C_8H_{16}	Dimethyl cyclo-hexanes (excluding 1, 1-)	6	107.4	88.8 (mean)	18.6
$C_{10}H_{18}$	Decahydronaphthalene (trans)	6, 6	129.4	89.4	40.0

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(7) "Selected Values of Properties of Hydrocarbons", Natl. Bureau of Standards; E. B. Wilson, JR., *Chem. Rev*.. **27**, 17 (1940); Landolt-Börnstein ; *Chem. Abst*.; "*Annual Review of Physical Chemistry*", **1**, (1950), Annual Reviews, Inc., Stanford, California ; S. Kaneko, "Thermodynamics", Tokyo, (1941).

the conclusion of Bremner-Thomas(4) from the atomic group method that in cyclohexane the entropy depression due to ring closure is about 20 e.u.

The values of resonance entropies of some substances are tabulated in Table 3. Many substances in the table have been interpreted by Pauling(8) as having resonance effects between various valence structures. The symbol $S^\circ_{\text{calc.}}$ is the calculated value for the same typical valence structure as in the case of the resonance energy. The small resonance entropy 1.4 e.u. of carbon monoxide indicates that in diatomic molecule the entropy does not decrease appreciably with the resonance effect.

Table 3

Resonance Entropy (unit, e. u.)

Substance		$S^\circ_{\text{calc.}}$	$S^\circ_{\text{obs.}}$	Resonance entropy
CH_3NO_2	Nitromethane	73.2	65.7	7.5
CH_2:CHCl	Vinyl chloride	65.0	61.1	3.9
CH_3COOH	Acetic acid	73.2	69.4	3.8
HCOOH	Formic acid	64.0	60.0	4.0
C_4H_6	1, 3-Butadiene	72.0	66.6	5.4
C_5H_8	1, 3-Pentadiene (trans) (Piperylene, trans)	81.2	76.4	4.8
〃	2-Methyl-1, 3-butadiene (Isoprene)	79.6	75.4	4.4
SF_6	Sulphur hexafluoride	83.9	69.4	14.5
CF_4	Carbon tetrafluoride	68.5	62.4	6.1
CCl_4	Carbon tetrachloride	76.9	74.2	2.7
CBr_4	Carbon tetrabromide	88.5	85.6	2.9
SiF_4	Silicon tetrafluoride	72.3	67.4	4.9
BF_3	Boron trifluoride	64.4	61.2	3.2
PF_3	Phosphorus trifluoride	68.6	64.1	4.5
AsF_3	Arsenic trifluoride	72.8	69.1	3.7
CF_3CH_3	1, 1, 1-Trifluoroethane	75.8	66.9	8.9
CCl_3CH_3	1, 1, 1-Trichloro ethane	82.3	77.0	5.3
CH_3NC	Methyl isocyanide	61.0	58.8	2.2
Cl_3PO	Trichlorophosphoxide	84.3	77.6	6.7
Cl_3PS	Trichlorophosphosulphide	86.6	79.3	7.3
$(CH_3)_2CO$	Acetone	73.2	70.1	3.1
$COCl_2$	Phosgene	72.9	69.1	3.8
SO_3	Sulphur trioxide	75.0	61.2	13.8
SO_2	Sulphur dioxide	64.5	59.4	5.1
CO_2	Carhon dioxide	60.9	50.2	10.7
CO	Carbon monoxide	47.0	45.6	1.4

As from thermodynamics

$$\Delta F=\Delta H-T\cdot\Delta S,$$

the degree of stabilization due to resonance effect must be originally discussed with the resonance free energy, but not only the resonance energy. In the extreme case as carbon dioxide the resonance entropy is 10.7 e. u. and the resonance energy is 33 kcal., so that the resonance free energy becomes

$$\Delta F=33,000-298\times 10.7$$
$$=33,000-3,189=29,811 \text{ (cal.)}$$

at ordinary temperature. In general case, however, the resonance entropy is not so large that it may be negligible compared with the resonance energy.

The substances, which have abnormal depressions due to ring closure and resonance effect, are aromatic compounds as shown in Table 4. As closure plus resonance entropy of benzene is 25.1 e.u. and closure entropy of benzene must be 20.9 e.u., taken as the same as cyclohexane, the resonance entropy of benzene becomes 4.2 e. u., which agrees well with the conclusion of Bremner-Thomas(4) that the depression of entropy due to resonance effect is about 4 e.u. in benzene.

Table 4

Closure plus Resonance Entropy (unit, e. u.)

Substance		$S^\circ_{\text{calc.}}$	$S^\circ_{\text{obs.}}$	Closure +reson. entropy
C_6H_6	Benzene	89.4	64.3	25.1
—	Alkyl benzenes	—	—	19.3 (mean)
C_8H_8	Styrene	105.4	82.5	22.9
C_9H_{10}	Methyl styrenes	—	—	21.7 (mean)

We have not seen any substance, which has the abnormal elevation of entropy, namely, for which the observed entropy is much larger than the entropy calculated by means of the present rule, excluding some exceptions in Table 1. From this fact it will be said that the present rule gives probably the upper limit of the observed entropy of gas molecule.

Bond Entropy

The quantity *Entropy of formation from atoms* S°_{af} was defined as

$$S^\circ_{af}=(\text{Entropy of atomic state})-(\text{Entropy of molecular state}), \quad (14)$$

with the analogy of enthalpy of formation from atoms. Entropy of atomic state becomes with the use of eq. (10)

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(8) L. Pauling, "The Nature of Chemical Bonds", Cornell Univ. Press, New York, 1940.

$$(\text{Entropy of atomic state}) = \sum^{n}(26+3/2\cdot R\ln X)$$

$$=26n+3/2\cdot R\ln\overset{n}{\Pi}(X), \qquad (15)$$

and entropy of molecular state becomes with the use of eq. (6)

$$(\text{Entropy of molecular state}) =$$

$$26+3/2\cdot R\ln\overset{n}{\Pi}(X)+0.7\ln\overset{m}{\Pi}\left(\frac{X+Y}{e^{\alpha}}\right). \qquad (16)$$

From these equations it follows

$$S^{\circ}{}_{af}=26(n-1)-0.7\ln\overset{m}{\Pi}\left(\frac{X+Y}{e^{\alpha}}\right).$$

As for the substances excluding those of ring structure

$$m=n-1, \qquad (8)$$

it follows

$$S^{\circ}{}_{af}=\sum^{m}\left\{26-0.7\ln\left(\frac{X+Y}{e^{\alpha}}\right)\right\} \qquad (17)$$

$$=\sum^{m}S^{\circ}{}_{B}, \qquad (18)$$

where

$$S^{\circ}{}_{B}=26-0.7\ln\left(\frac{X+Y}{e^{\alpha}}\right). \qquad (19)$$

Although the quantity $S^{\circ}{}_{B}$ has the additivity as shown in eq. (18), it has not the independency as shown in eqs. (19) and (7). Namely $S^{\circ}{}_{B}$ has, besides the quantities X, Y and N, which are proper to the bond, the quantities n, m, B, n_X and f, which are controlled with the situations of the bond. Consequently it is impossible to build up *true bond entropy*, which has both the additivity and the independency as in the case of bond energy, although it is possible to build up *formal bond entropy* $S^{\circ}{}_{B}$, which has only the additivity as stated above. It is, therefore, also impossible to construct the bond free energy with the sufficient accuracy.

In the special case such as non-branched hydrocarbon involving more than two carbon atoms, excluding ethylene and acethylene, $n\geqq 5$, $B=0$, $n_X=0$ and $f=0$ as stated above, so that eq. (7) becomes

$$\alpha=-\frac{15.7}{m}+1.9^{N}, \qquad (20)$$

and eq. (17) becomes

$$S^{\circ}{}_{af}=\sum^{m}\left\{26-0.7\ln\left(\frac{X+Y}{1.9^{N}}\right)\right\}-11 \qquad (21)$$

$$=\sum^{m}S^{\circ}{}_{B}{}'-11,$$

where $S^{\circ}{}_{B}{}'$ is defined as

$$S^{\circ}{}_{B}{}'=26-0.7\ln\left(\frac{X+Y}{1.9^{N}}\right). \qquad (22)$$

It follows therefore

$$S^{\circ}{}_{af}+11=\sum^{m}S^{\circ}{}_{B}{}'. \qquad (23)$$

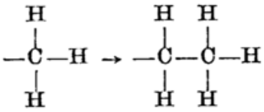
As shown in eqs. (22) and (23) $S^{\circ}{}_{B}{}'$ has both the independency and the additivity. However the quantity $S^{\circ}{}_{B}{}'$ is also not suitable for the name bond entropy, because the range of application of this quantity is very small, and furthermore the meaning of the additivity of this quantity is not clear-cut in the physical sense as shown in eq. (23).

Derivation of Atomic Group Method

Many rules in the atomic group method must be included naturally in the present rule. The typical rules of the atomic group displacement method, for example, are derived as follows:

(1) Displacement of H of C—H with CH_3 (excluding $C_1\rightarrow C_2$)

(a) Non-branched



increase: (C, H, H); (C−H×2, C−C×1)

decrease: ....

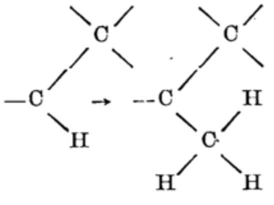
From eq. (13) the increase of entropy by displacement ΔS° is calculated as

$$\Delta S^{\circ}=2.98\times\ln 12+0.7\times\{2\ln 13+\ln 24\}-1.33\times 3$$

$$=7.4+5.8-4.0=9.2,$$

while the observed mean value of ΔS° is 9.2 e.u.

(b) Branched with two degree



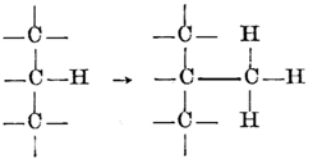
From eqs. (6) and (7)

$$\Delta S^{\circ}=9.2(\text{calculated value in la})-0.7\times\frac{2^2}{1.8}$$

$$=9.2-1.6=7.6,$$

while the observed mean value is 7.5 e. u.

(c) Branched with three degree



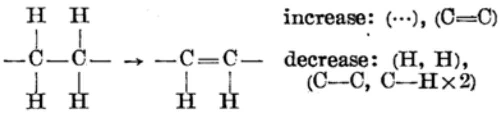
From eqs. (6) and (7)

$$\Delta S^{\circ}=9.2(\text{calculated value in la})-0.7\times\left\{-\frac{2^2}{1.8}+\frac{3^2}{1.8}\times 2\right\}$$

$$=9.2+1.6-3.5\times 2=3.8,$$

while the observed mean value is 3.8 e.u.

(2) Displacemens of C—C with C=C (excluding ethane to ethylene)



increase: (···), (C=C)

decrease: (H, H), (C—C, C—H×2)

From eqs. (6) and (7)

$$\Delta S^{\circ}=-2\times\{0.7\ln 13-0.7\times 1.9\}$$
$$=-2\times(1.8-1.3)=-1.0,$$

while the observed mean value is -1.0 e.u.

The calculated values of ΔS° as stated above are very convenient for the calculation of S° of hydrocarbons, and are applicable also for the substances involving the abnormal depressions, provided that the latter are not affected by the displacement.

Activation Entropy of Chemical Reaction

According to Eyring et al.(9) the specific reaction rate of bimolecular gas reaction k is expressed by the equation:

$$\mathrm{k}=\kappa e^{2}\frac{kT}{h}RTe^{\Delta S_{p}^{*}/R}e^{-E/RT}\ (\text{cc.mole}^{-1}\text{sec.}^{-1}), \tag{24}$$

where κ is the transmission coefficient, k is Boltzman constant (1.372×10^{-16} erg·degree^{-1}), h is Planck constant (6.554×10^{-27} erg.sec.), R is universal gas constant (in the terms $e^{\Delta S_p^*/R}$ and $e^{-E/RT}$ R is 1.987 cal·degree^{-1}, and in the term RT, R is 82.06 cc·atm·degree^{-1}), ΔS_p^* is activation entropy when the standard state is chosen as 1 atm., and E is the experimental activation energy. Compared with Arrhenius's equation

$$\mathrm{k}=Ae^{-E/RT},$$

the frequency factor A is expressed as

$$A=\kappa e^{2}\frac{kT}{h}RTe^{\Delta S_{p}^{*}/R}. \tag{25}$$

Putting $\kappa=1$, and introducing the numerical values, it follows

$$A=1.27\times10^{13}\,T^{2}e^{\Delta S_{p}^{*}/2}\ (\text{cc}\cdot\text{mole}^{-1}\text{sec.}^{-1}). \tag{26}$$

If ΔS_p^* is given, therefore, the frequency factor of bimolecular gas reaction can be calculated readily with the use of eq. (26)

Activation entropy ΔS_p^* is given from thermodynamics by

$$\Delta S_{p}^{*}=\Delta S_{p}^{\circ *}+\Delta C_{p}^{*}\ln\frac{T}{298}, \tag{27}$$

where $\Delta S_p^{\circ *}$ is entropy difference between activated complex and initial state at 298°K and 1 atm., and ΔC_p^* is the difference of molecular heat at constant pressure between activated complex and initial state assuming independent with temperature.

When the initial state converts to activated complex, molecular heat will decrease on the one hand according to the presumed decrease of degrees of freedom of translation and rotation, and will increase on the other hand according to the presumed increase of degrees of freedom of vibration and depressions of vibrational frequencies. As these problems are too complicated to discuss quantitatively, it was assumed that these opposite effects cancel each other, i. e.,

$$\Delta C_{p}^{*}=0. \tag{28}$$

For bimolecular reaction $\Delta S_p^{\circ *}$ is expressed as

$$\Delta S_{p}^{\circ *}=S^{\circ *}-(S^{\circ}_{A}+S^{\circ}_{B}), \tag{29}$$

where $S^{\circ *}$, S°_A and S_B° are S° of activated complex, reactant A, and reactant B respectively. S°_A and S°_B can readily be computed by means of the present rule, if the reactants have not abnormal depressions. Compared with the entropies of normal molecules, entropy of activated complex will increase on the one hand according to the presumed elongation of the bond distance and depression of vibrational frequency, and will decrease on the other hand according to the presumed restrictions by the activated bonds(10) and depressions by ring closure and resonance effect. As these effects are too complicated to discuss quantitatively, it was assumed that the entropies of the activated complexes of the triatomic reaction

$$\mathrm{X+Y-Z}\rightleftarrows \underbrace{\mathrm{X\cdots Y\cdots Z}}\dashrightarrow \mathrm{X-Y+Z},$$

and the double decomposition

could be computed with the models

X—Y—Z and

respectively, as the result of cancellation of both effects.

The frequency factors of some simple reactions computed by means of the above-mentioned series of assumptions were compared with the observed values in Table 5. As seen in the table the calculated values agree with the observed within 3∼1/6 times, so that the rough assumptions above stated concerning the molecular heat and entropy of

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(9) S. Glasstone, K. J Laidler and H. Eyring. "The Theory of Rate Processes", McGraw-Hill, Inc., New York, 1941.

(10) K. Otozai, This Bulletin. **24**, 218 (1951); K. Otozai, *Scient. Papers, Osaka Univ.*, No. 20, (1951).

Table 5

Calculation of Frequency Factor

Reaction	$S^{\circ *}$ (e. u.)	S°_A (e. u.)	S°_B (e. u.)	ΔS^*_p (e. u.)	T (°K)	$A_{\text{calc.}}$ (cc·mole^{-1}·sec^{-1})	$A_{\text{obs.}}$ (cc·mole^{-1}·sec^{-1})	$A_{\text{calc.}}/A_{\text{obs.}}$
$H+H_2=H_2+H$	33.2	26.0	29.5	−22.3	300	1.6×10^{13}	1.1×10^{13}(9)	1
$Cl+H_2=ClH+H$	45.9	36.7	29.5	−20.3	298	0.5×10^{14}	1.8×10^{14}(9)	1/4
$H+HBr=H_2+Br$	48.8	26.0	45.2	−22.4	500	4.3×10^{13}	1.3×10^{13}(9)	3
$Br+H_2=BrH+H$	48.8	39.1	29.5	−19.8	499	1.6×10^{14}	0.8×10^{14}(9)	2
$H_2+I_2=2HI$	70.1	29.5	61.9	−21.3	700	1.5×10^{14}	2.0×10^{14}(11)	1
$Br_2+Cl_2=2BrCl$	90.8	58.7	53.2	−21.1	—	0.3×10^{14} (298°K)	1.8×10^{14}(12) (room)	1/6
$H_2C{:}CH_2$ $+H_2=C_2H_6$	54.7	52.7	29.5	−27.5	773	0.8×10^{13}	1.9×10^{13}(13)	1/2

activated complex are approximately correct. This discussion concerning entropy of activation is one of two works of the research on activation energy performed by one of the authors.(10)

Summary

(1) From the standpoint of chemical bond a new empirical rule for the calculation of entropy of polyatomic gas molecule has been proposed. It agrees with the observed value within the error of ±2 e. u., and includes monoatomic and diatomic molecule as a special case, and finally gives the upper limit of the observed value.

(2) The abnormal depression of entropy from the standard of the present rule was interpreted as ring closure entropy and resonance entropy, and respective values were given for some typical substances. Closure entropy 20.9 e. u. of cyclohexane and resonance entropy 4.2 e. u. of benzene agreed well with the conclusion of Bremner-Thomas according to the atomic group method.

(3) It has been shown that resonance entropy is so small that its contribution to the resonance free energy is neglisible compared with resonance energy. In special case, however, the contribution of the resonance entropy is about 10% of the resonance free energy, as in the case of carbon dioxide.

(4) It has been shown that it is impossible to construct the true bond entropy, which is additive and independent. But it is possible to build up the formal bond entropy, which is additive and not independent.

(5) In order to show that the present rule includes naturally the atomic group method, some typical rules of the atomic group displacement method have been derived.

(6) Under some assumptions the frequency factors of some simple chemical reactions have been computed by means of the present rule. The calculated values agreed with the observed within 3∼1/6 times.

The authors wish to express their sincere thanks to Prof. T. Titani for his valuable discussions of these problems, and to Dr. S. Seki for his kind guidance concerning thermochemical data.

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(11) M. Bodenstein, *Z. phys. Chem.*, **29**, 295 (1899).

(12) W. Jost, *Z. phys. Chem.*, B **14**, 413 (1931).

(13) R. N. Pease, *J. Am. Chem. Soc.*, **54**, 1876 (1932).