rings are bound with greater energy in $Ru(C_5H_5)_2$ is seen by comparing the ring–metal–ring symmetric stretching frequencies of $Fe(C_5H_5)_2$ and $Ru(C_5H_5)_2$ which appear at 303 and 330 cm.$^{-1}$, respectively. Corresponding increases in several other frequencies occur with the result that the increase in molecular weight of $Ru(C_5H_5)_2$ is compensated completely by the higher set of frequencies resulting from increased stability. Actually the calculated S^0 for $Ru(C_5H_5)_2$ is slightly less than that for $Fe(C_5H_5)_2$.

A comparison of the thermodynamic functions of $Ni(C_5H_5)_2$ with $Fe(C_5H_5)_2$ are significantly different. Since these compounds have nearly the same molecular weight, this difference is due to the much greater stability of $Fe(C_5H_5)_2$.

Acknowledgment.—The authors wish to thank the Research Corporation for a grant-in-aid supporting this work; and Dr. J. C. Brantley of Linde Air Products Company for supplying us with a sample of bis-cyclopentadienylnickel (II).

MANHATTAN, KANSAS

[CONTRIBUTION NO. 49 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

2,3-Dimethyl-2-butene: Thermodynamic Properties in the Solid, Liquid and Vapor States

BY D. W. SCOTT, H. L. FINKE, J. P. MCCULLOUGH, M. E. GROSS, J. F. MESSERLY, R. E. PENNINGTON AND GUY WADDINGTON

RECEIVED MAY 19, 1955

Various thermodynamic properties of 2,3-dimethyl-2-butene were studied experimentally. The entropy of the liquid a 298.16°K. (S_{satd} = 64.58 cal. deg.$^{-1}$ mole^{-1}) was computed from calorimetric values of the heat capacity in the solid and liquid states (11 to 318°K.) and of the heats of transition and fusion (844 cal. mole^{-1} at 196.82°K. and 1542 cal. mole^{-1} at the triple point, 198.92°K., respectively). Results obtained for the heat capacity of the liquid (C_{satd}), vapor pressure (p), heat of vaporization (ΔH_v), heat capacity in the ideal gas state (C_p°), and the second virial coefficient [$B = (PV - RT)/P$] are represented as a function of temperature by the following empirical equations: (1) $C_{satd} = 48.178 - 0.16068T + 6.2188 \times 10^{-4}T^2 - 5.2083 \times 10^{-7} T^3$, cal. deg.$^{-1}$ mole^{-1}) (200–320°K.); (2) $\log_{10}p$ (mm.) $= 6.93324 - 1206.037/(t + 224.400)$, (29–73°); (3) $\Delta H_v = 10,674 - 5.713T - 0.01344T^2$, cal. mole^{-1} (292–346°K.); (4) $C_p^\circ = 4.454 + 0.087361T - 1.1983 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1} (334–473°K.); and $B = -2764 - 4.93 \exp.(1100/T)$, cc. mole^{-1} (292–473°K.). The entropy in the ideal gas state at 298.16°K. (S° = 87.16 cal. deg.$^{-1}$ mole^{-1}) was computed from these data. A vibrational assignment was made for 2,3-dimethyl-2-butene, and the average height of the potential barriers hindering internal rotation of the methyl groups, 680 cal. mole^{-1}, was evaluated from the calorimetric data. Values of the functions $(F^\circ - H_0^\circ)/T$, $(H^\circ - H_0^\circ)/T$, $H^\circ - H_0^\circ$, S° and C_p° were calculated at selected temperatures to 1500°K.

As part of the continuing program of this Laboratory to measure thermodynamic properties of hydrocarbons important in petroleum technology, calorimetric studies were made on 2,3-dimethyl-2-butene. These included determination of the entropy of the vapor from Third Law studies and measurement of the heat capacity of the vapor. The methods of statistical mechanics were used to compute thermodynamic functions for the ideal gas state.

Experimental

The 1951 International Atomic Weights[1] and the 1951 values of the fundamental physical constants[2] were used for all computations described in this paper. Measurement of temperature above 90°K. was made in terms of the International Temperature Scale of 1948,[3] and International Celsius temperatures were converted to Kelvin temperatures by adding 273.16°. Below 90°K., the temperature scale was defined by a platinum resistance thermometer calibrated at the National Bureau of Standards in terms of the provisional scale established by Hoge and Brickwedde.[4] All electrical and mass measurements were referred to standards calibrated at the National Bureau of Standards. Energy measured in joules was converted to calories by use of the definitions 1 cal. = 4.1840 abs. j. = 4.1833 int. j.

Material.—The 2,3-dimethyl-2-butene used for low temperature calorimetry and for measurement of vapor pressure was an A.P.I. Research sample.[5] In calorimetric melting point studies, this sample was found to contain 0.05 mole % liquid-soluble, solid-insoluble impurity. A second sample, of somewhat lower purity (about 99.5 mole %), supplied by A.P.I. Research Project 6, was used for the measurements of heat of vaporization and vapor heat capacity, which required a larger sample than the other studies. The samples of 2,3-dimethyl-2-butene were received in sealed ampoules with internal break-off tips and were stored in the dark at 5°. Transfers to appropriate receivers were made by vacuum distillation. At no time in the handling of the material or in the experiments were the samples in contact with gases other than helium. Such precautions were necessary to avoid oxidation of 2,3-dimethyl-2-butene by atmospheric oxygen. In the studies of heat of vaporization and vapor heat capacity, 0.02 mole % hydroquinone was added to the sample as inhibitor.

The Heat Capacity in the Solid and Liquid States.—The low temperature thermal properties of 2,3-dimethyl-2-butene were measured in an adiabatic cryostat similar to that described by Ruehrwein and Huffman.[6] The sample (about 0.44 mole) was sealed in a copper calorimeter that contained horizontal perforated disks to facilitate attainment of thermal equilibrium and prevent settling of the solid phase during fusion experiments. The observed values of heat capacity at saturation pressure (C_{satd}) of the solid and liquid are presented in Table I. The temperature increments used in the experiments were small enough that corrections for non-linear variation of C_{satd} with T were unnecessary (the

---

(1) E. Wichers, THIS JOURNAL, **74**, 2447 (1952).

(2) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

(3) H. F. Stimson, *J. Research Natl. Bur. Standards*, **42**, 209 (1949).

(4) H. J. Hoge and F. G. Brickwedde, *ibid.*, **22**, 351 (1939).

(5) This sample, made available through the American Petroleum Institute Research Project 44 on the "Collection, Analysis, and Calculation of Data on Properties of Hydrocarbons," was purified by the American Petroleum Institute Research Project 6 on the "Analysis, Purification, and Properties of Hydrocarbons," from material supplied by the General Motors Corporation, Detroit, Michigan.

(6) R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943).

increments employed were approximately 10% of the absolute temperature below 50°K., 5 to 6° from 50 to 100°K., and 6 to 10° above 100°K.). The precision of the heat capacity measurements was usually within ±0.1%; above 30°K. the accuracy uncertainty of the values of C_{satd} should not exceed 0.2%. The following equation represents the smoothed values of heat capacity for the liquid (Table III) within ±0.03 cal. deg.$^{-1}$ mole^{-1} in the range 200 to 320°K.

$$C_{satd}(\text{liq.}) = 48.178 - 0.16068T + 6.2188 \times 10^{-4}T^2 - 5.2083 \times 10^{-7}T^3 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (1)$$

TABLE I

THE MOLAL HEAT CAPACITY OF 2,3-DIMETHYL-2-BUTENE IN CAL. DEG.$^{-1}$

T, °K.[a]	C_{satd}[b]	T, °K.[a]	C_{satd}[b]	T, °K.[a]	C_{satd}[b]
Crystals I		62.98	14.493	176.04	32.063
		68.25	15.706	185.48	33.864[c]
11.60	0.525	73.49	16.806	193.47	37.220[c]
11.80	.551	77.80	17.683		
13.05	.760	78.81	17.901	Crystals II (No exptl. values)	
13.07	.771	83.83	18.916		
14.63	1.065	84.34	19.012		
14.94	1.119	85.06	19.159		
16.55	1.463	90.47	20.124	Liquid	
17.18	1.616	90.73	20.085		
18.84	2.028	96.55	21.095	204.25	36.86
19.55	2.216	97.15	21.206	208.99	36.99
21.51	2.756	102.52	22.035	211.49	37.08
22.03	2.908	103.07	22.064	211.76	37.07
24.32	3.631	104.50	22.344	219.56	37.34
24.86	3.796	108.24	22.883	222.41	37.46
27.13	4.429	110.54	23.198	228.45	37.70
27.85	4.652	112.10	23.457	237.25	38.10
29.92	5.297	114.88	23.841	246.80	38.56
30.78	5.558	118.61	24.339	257.10	39.11
33.86	6.541	123.11	24.945	267.25	39.71
37.60	7.697	127.60	25.518	277.25	40.34
41.77	8.930	137.14	26.710	287.10	40.99
46.04	10.148	146.27	27.853	295.57	41.58
50.57	11.412	149.98	28.331	297.21	41.69
55.31	12.620	155.06	28.984	302.69	42.08
57.68	13.217	160.09	29.658	307.56	42.43
59.91	13.765	163.92	30.156	318.14	43.23

[a] T is the mean temperature of each heat capacity measurement. [b] C_{satd} is the heat capacity of the condensed phase under its own vapor pressure. [c] Not corrected for heterophase premelting.

The Transition Temperature, Triple Point and Sample Purity.—An isothermal transition was found to occur in crystalline 2,3-dimethyl-2-butene about 2° below the melting point. Equilibrium temperatures were observed with varying amounts of the solid transposed to the high temperature form (crystals II) with the following results.

% Crystals II	11	48	81
Equilibrium temp. °K.	196.814	196.817	196.819

The transition temperature was taken to be 196.82°K.

The triple point and sample purity were determined in a calorimetric study of the equilibrium temperature as a function of the fraction of sample melted.[7] The results of this study are presented in Table II. The equilibrium melting temperatures, T_{obsd}, were plotted against the reciprocal of the fraction melted, $1/F$. The triple point temperature, $T_{T.P.}$, was determined by linear extrapolation of these data to $1/F = 0$. The mole fraction of total impurity in the sample, N_2^*, was calculated by the relationship $N_2^*/F = A(T_{T.P.} - T_{obsd})$, where A is the first cryoscopic constant, $\Delta H_{fusion}/RT^2_{T.P.}$. This procedure is based on the assumptions that ideal solutions are formed in the liquid phase and that the impurity is insoluble in the solid phase.

TABLE II

2,3-DIMETHYL-2-BUTENE: MELTING-POINT SUMMARY

Heat of fusion, $\Delta H_{fusion} = 1542$ cal. mole^{-1}; triple point, $T_{T.P.} = 198.92 \pm 0.05°K.$; cryoscopic constant, $A = 0.0196$ deg.$^{-1}$; impurity = 0.05 ±0.1 mole %.

Melted, %	$1/F$	T, °K. Obsd.	T, °K. Graph.[b]
18.20	5.49	198.7984	198.7925
30.70	3.26[a]	.8462[a]	.8462
53.75	1.860	.8805	.8798
73.03	1.369	.8912	.8918
92.31	1.083[a]	.8984[a]	.8984
100.00	1.000		.9004
Pure	0.000		198.9244[c]

[a] A straight line through these points was extrapolated to $1/F = 0$ to obtain the triple point temperature, $T_{T.P.}$. [b] Temperatures read from the straight line of footnote a. [c] Triple point temperature.

The Heats of Transition and Fusion.—Two measurements were made of the enthalpy change over temperature intervals that included both the transition temperature and the triple point. The input of energy to the calorimeter was interrupted for a determination of the equilibrium temperature after enough energy had been introduced to completely transpose crystals I to crystals II. Subtraction of the energy absorbed as $\int C_{satd}\,dT$ for crystals I and liquid gave values for the sum of the heat of transition, heat of fusion and $\int_{196.82}^{198.92} C_{satd}\,dT$ for crystals II. The values obtained were 2462.5 and 2460.5 cal. mole^{-1}. Division of the sum among the three quantities of which it was comprised was somewhat arbitrary, as accurate values could not be obtained for the heat capacity of crystals II because of the extremely short temperature range and large premelting effect. A constant value of 36 cal. deg.$^{-1}$ mole^{-1} was taken for the heat capacity of crystals II, and the following values of the heats of transition and fusion were calculated.

Heat of fusion: 842.7, 845.4; average 844.0 cal. mole^{-1}

Heat of fusion: 1544.2, 1539.4; average 1541.8 cal. mole^{-1}

The arbitrariness in the division of the total enthalpy has an insignificant effect on the value of the entropy change calculated over a temperature interval that includes the transition temperature and triple point.

The Thermodynamic Properties in the Solid and Liquid States.—Values of the entropy, heat content and free energy function in the solid and liquid states at saturation pressure were computed from the thermal data presented in the foregoing sections. The results at selected temperatures from 10 to 320°K. are presented in Table III. These values were computed by appropriate numerical integration of values of C_{satd} read at integral temperatures from a large scale plot of the data of Table I. A Debye function for 6 degrees of freedom with $\theta = 138.7°$ was used for extrapolation below 11°K. Corrections for the effects of heterophase premelting have been applied to the data in Table III.

The Vapor Pressure.—The vapor pressure from 29 to 73° was measured with the twin ebulliometer system described in an earlier publication from this Laboratory.[8] The boiling and condensation temperatures of water and 2,3-dimethyl-2-butene were measured as both compounds were boiled simultaneously at the same pressure. The "observed" vapor pressure values, presented in Table IV, were obtained from the vapor pressure data for water given by Osborne, Stimson and Ginnings.[9] At both the beginning and the end of the measurements, the difference between the boiling and condensation temperatures of the sample was 0.003–0.004° at 760 mm. pressure. This small, constant difference is evidence that the sample was essentially free of impurity of different volatility and that no change in purity occurred during the measurements. An Antoine equation, eq. 2, was obtained from the data of Table IV by a least squares adjustment.[10] The last column of Table III lists the differ-

---

(7) S. S. Todd, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **69**, 1519 (1947).

(8) G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, *ibid.*, **71**, 797 (1949).

(9) N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

(10) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *ibid.*, **35**, 219 (1945).

TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF 2,3-DIMETHYL-2-BUTENE IN THE SOLID AND LIQUID STATES[a]

T, °K.	$-(F_{satd} - H_0^\circ)/T$, cal. deg.$^{-1}$	$(H_{satd} - H_0^\circ)/T$, cal. deg.$^{-1}$	$H_{satd} - H_0^\circ$, cal.	S_{satd}, cal. deg.$^{-1}$	C_{satd}, cal. deg.$^{-1}$
			Crystals I		
10	0.029	0.087	0.868	0.116	0.347
15	.098	.289	4.340	.387	1.139
20	.226	.643	12.865	.869	2.335
25	.419	1.128	28.204	1.547	3.832
30	.675	1.699	50.98	2.374	5.308
35	.983	2.329	81.51	3.312	6.890
40	1.337	2.994	119.77	4.331	8.395
45	1.729	3.675	165.39	5.404	9.845
50	2.151	4.364	218.18	6.515	11.258
60	3.068	5.726	343.5	8.794	13.778
70	4.050	7.043	492.9	11.093	16.075
80	5.073	8.301	664.0	13.374	18.145
90	6.121	9.504	855.3	15.625	20.052
100	7.182	10.640	1064.0	17.822	21.650
110	8.247	11.709	1288.0	19.956	23.141
120	9.309	12.721	1526.5	22.030	24.535
130	10.365	13.680	1778.3	24.045	25.820
140	11.413	14.591	2042.7	26.004	27.064
150	12.449	15.465	2319.6	27.914	28.332
160	13.475	16.309	2609.4	29.784	29.630
170	14.48	17.133	2912.6	31.62	31.06
180	15.49	17.953	3231	33.44	32.73
190	16.48	18.781	3568	35.26	34.65
196.82	17.15	19.354	3809	36.51	36.00
			Crystals II		
196.82	17.15	23.642	4653	40.79	36
198.92	17.40	23.773	4728	41.18	36
			Liquid		
198.92	17.40	31.52	6270	48.93	36.72
200	17.57	31.55	6310	49.13	36.75
210	19.12	31.80	6678	50.92	37.02
220	20.60	32.04	7050	52.65	37.35
230	22.03	32.28	7426	54.32	37.77
240	23.41	32.52	7806	55.94	38.23
250	24.75	32.76	8191	57.51	38.73
260	26.04	33.00	8581	59.04	39.27
270	27.29	33.24	8976	60.53	39.87
273.16	27.67	33.32	9103	61.00	40.07
280	28.50	33.49	9378	62.00	40.51
290	29.68	33.74	9787	63.43	41.18
298.16	30.62	33.96	10125	64.58	41.75
300	30.83	34.00	10202	64.84	41.88
310	31.95	34.27	10625	66.22	42.60
320	33.04	34.54	11055	67.59	43.37

[a] The values tabulated are the free energy function, heat content function, heat content, entropy and heat capacity of the condensed phases at saturation pressure.

ences between the observed values and those calculated from eq. 2. The normal boiling point from eq. 2 is 73.21°.

$$\log_{10} p = 6.93324 - 1206.037/(t + 224.400) \quad (p \text{ in mm. and in } t\ ^\circ\text{C.}) \quad (2)$$

The Heat of Vaporization.—The heat of vaporization and vapor heat capacity were determined in the flow calorimeter system previously described.[11] A metal vaporizer replaced the glass vaporizer described in ref. 11, but the principle of operation remained the same. Measurements of the heat of vaporization were made at four temperatures that corresponded to vapor pressures of $^1/_8$, $^1/_4$, $^1/_2$ and 1 atm. The results of these experiments are recorded in Table V. The accuracy uncertainty of the values of heat of vaporization should not exceed 0.1%. The following empirical equation represents the experimental data within ±2 cal. mole^{-1}

TABLE IV

THE VAPOR PRESSURE OF 2,3-DIMETHYL-2-BUTENE

Boiling point, °C. Water	Boiling point, °C. 2,3-Dimethyl-2-butene	Pressure, mm. Obsd.	Pressure, mm. Obsd. − Calcd.[a]
60.000	29.026	149.41	+0.02
65	34.404	187.57	−0.02
70	39.820	233.72	−0.01
75	45.278	289.13	0.00
80	50.778	355.22	+0.01
85	56.321	433.56	+0.02
90	61.909	525.86	−0.01
95	67.535	633.99	+0.03
100	73.208	760.00	+0.02

[a] Calculated from eq. 2.

$$\Delta H_v = 10{,}674 - 5.713T - 0.01344T^2, \quad \text{cal. mole}^{-1}\ (292\text{–}346^\circ\text{K.}) \quad (3)$$

TABLE V

THE MOLAL HEAT OF VAPORIZATION AND GAS IMPERFECTION OF 2,3-DIMETHYL-2-BUTENE

T, °K.	No. expts.	ΔH_v, cal.	Bobsd., cc.	Bcalcd.,[a] cc.
292.13	2	7856 ± 2[b]	−2179	−2214
307.87	3	7641 ± 2	−1818	−1875
325.79	3	7386 ± 1	−1596	−1589
346.37	3	7083 ± 3	−1362	−1351

[a] Calculated from eq. 5. [b] Maximum deviation of the experimental results from the mean.

The Vapor Heat Capacity.—Measurements of the vapor heat capacity were made at 2 or more pressures at each of 5 temperatures between 334 and 473°K. The results are listed in Table VI. Values of the heat capacity in the ideal gas state, C_p°, were determined from the data at finite pressures by linear extrapolations to zero pressure. It is estimated that the accuracy uncertainty of these values of C_p° is less than 0.2%. The following empirical equation represents the experimental values of C_p° within 0.04 cal. deg.$^{-1}$ mole^{-1}

$$C_p^\circ = 4.454 + 0.087361T - 1.1983 \times 10^{-5}T^2, \quad \text{cal. deg.}^{-1}\text{ mole}^{-1}\ (334\text{–}473^\circ\text{K.}) \quad (4)$$

TABLE VI

THE MOLAL VAPOR HEAT CAPACITY OF 2,3-DIMETHYL-2-BUTENE IN CAL. DEG.$^{-1}$

T, °K.	334.20	355.25	393.20	433.20	473.20
C_p (760 mm.)		35.048	37.577	40.407	43.350
C_p (380 mm.)	33.034	34.466			
C_p (250 mm.)			37.165	40.179	43.183
C_p (190 mm.)	32.686	34.221			
C_p° (obsd.)	32.34	33.94	36.96	40.07	43.10
C_p° (calcd.)[a]	32.29	33.94	36.94	40.08	43.10
$(\partial C_p/\partial P)_T$-(obsd.)	1.39	1.10	0.61	0.34	0.25
$(\partial C_p/\partial P)_T$-(calcd.)[b]	1.52	1.07	0.61	0.37	0.24

[a] Calculated from spectroscopic and molecular structure data. [b] Calculated by use of eq. 5; units of $(\partial C_p/\partial P)_T$ are cal. deg.$^{-1}$ mole^{-1} atm.$^{-1}$

Gas Imperfection and the Second Virial Coefficient.—The experimental heat of vaporization and vapor pressure data were used to compute values of the second virial coefficient, $B = (PV - RT)/P$, from the Clapeyron equation in

---

[11] G. Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947).

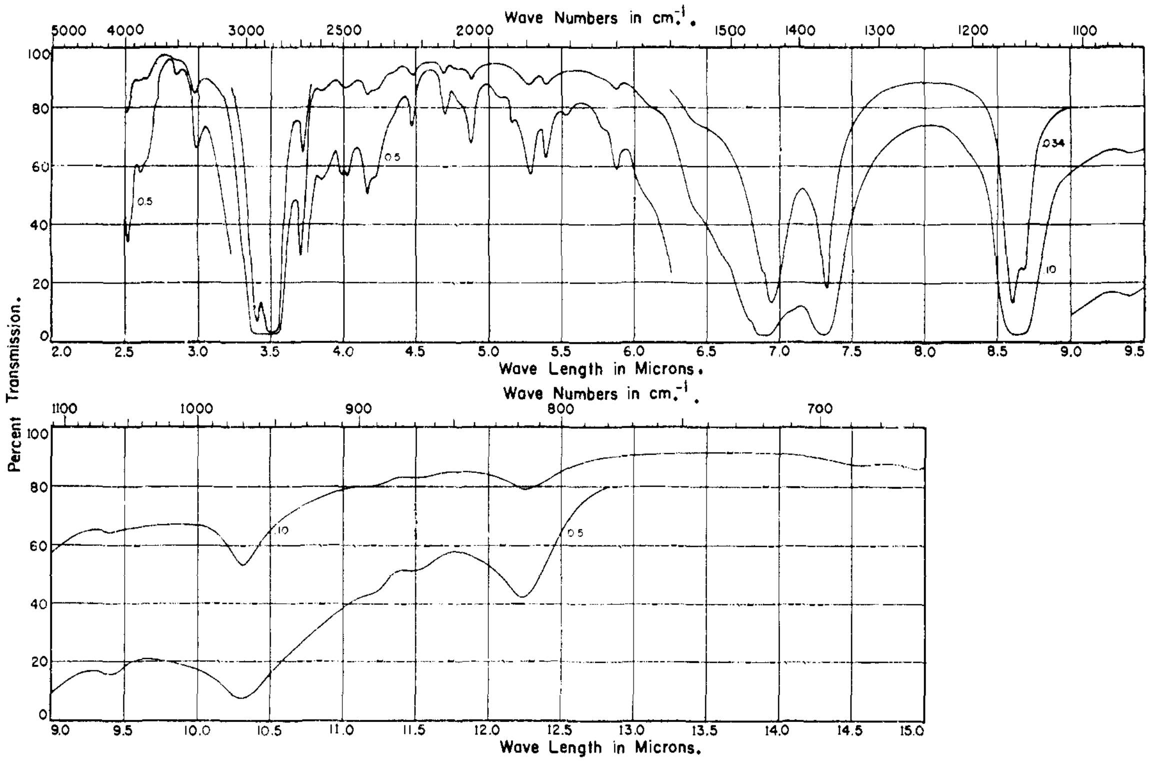

Fig. 1.—Infrared spectrum of 2,3-dimethyl-2-butene.

the form $B = [\Delta H_v/T(dP/dT)] - RT/P + V_L$, where V_L is the molal volume of the liquid. Values of (d^2B/dT^2) were calculated from the observed pressure dependence of the vapor heat capacity by use of the relationship $(\partial C_p/\partial P)_T = -T(\partial^2 V/\partial T^2)_P = -T(d^2B/dT^2)$. These values for B and its second derivative with respect to temperature were correlated by means of the empirical equation

$$B = -276 - 44.93 \exp(1100/T),\quad \text{cc. mole}^{-1}\ (292\text{-}473°\text{K.}) \quad (5)$$

where T is in °K.; the numerical constants were evaluated by methods outlined in an earlier paper.[12] Values of B and $(\partial C_p/\partial P)_T$ obtained from the experimental data and those calculated from eq. 5 are compared in Tables V and VI, respectively.

TABLE VII

THE MOLAL ENTROPY OF 2,3-DIMETHYL-2-BUTENE, CAL. DEG.$^{-1}$

0–12°K.	Extrapolation, $2D(138.7/T)$	0.200
12–196.82°	Crystals I, "graphical" $\int C_{\text{satd}}\, d \ln T$	36.306
196.82°	Transition, 844.0/196.82	4.288
196.82–198.92°	Crystals II, "graphical" $\int C_{\text{satd}}\, d \ln T$	0.381
198.92°	Fusion, 1541.8/198.92	7.751
198.92–298.16°	Liquid, "graphical" $\int C_{\text{satd}}\, d \ln T$	15.652
S_{satd} liq., 298.16°K. (±0.10)		64.58

T, °K.	292.13	307.87	325.79	346.37
S_{satd}, liq. (±0.10)	63.73[a]	65.93[a]	68.37[b]	71.10[b]
$\Delta H_v/T$[c]	26.90	24.82	22.67	20 45
$P(dB/dT)$[d]	0.07	0.11	0.17	0.24
$R \ln (p/760)$[e]	−4.13	−2.76	−1.38	0.00
$S°$, gas (obsd.) (±0.15)	86.57	88.10	89.83	91.79
$S°$, gas (calcd.)[f]	86.55	88.11	89.86	91.85

[a] Interpolated from Table III. [b] Extrapolated by use of eq. 1. [c] Entropy of vaporization; from Table V. [d] Entropy of gas imperfection; from eq. 5. [e] Entropy of compression; from eq. 2. [f] Calculated from spectroscopic and molecular structure data.

The Entropy.—Values of the entropy in the ideal gas state, $S°$, were computed from the data given in previous sections. The results are summarized in Table VII. The interpolated value at 298.16°K. is 87.16 ± 0.15 cal. deg.$^{-1}$ mole^{-1}.

Calculation of Thermodynamic Functions

The Vibrational Assignment.—The thermodynamic functions of 2,3-dimethyl-2-butene were computed by appropriate methods of statistical mechanics. The vibrational assignment was based on the spectroscopic data listed in Table VIII The sources of these data are: Raman spectrum from the work of Collins,[13] infrared spectrum from 14 to 38 μ from the A.P.I. tables,[14] and infrared spectrum from 2 to 14 μ from the spectrogram (Fig. 1) obtained by L. Mikkelsen of this Station. Results of earlier investigators[15] were also considered. These spectroscopic data were interpreted for a structure with a planar carbon skeleton and V_h symmetry. Only three weak frequencies in the spectra of the liquid (italicized in Table VIII) violate the strict vapor phase selection rules for V_h symmetry.

As a guide to interpretation of the spectroscopic data, approximate normal coördinate calculations were made. The C–H stretching and methyl bending frequencies were factored out of the matrix equations, and the same force constants were

---

[12] D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *J. Chem. Phys.*, **15**, 565 (1947).

[13] Russell Lewis Collins, Thesis, University of Oklahoma, 1953

[14] American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Infrared Spectral Data, Serial No. 1257.

[15] (a) T. Hayashi, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*), **25**, 31 (1934); (b) L. Piaux and M. Bourguel, *Ann. Chim.*, [11] **4**, 147 (1935); (c) J. Guy and J. Lecomte, *Bull. soc. chim. France*, 977 (1947); (d) W. G. Braun, D. F. Spooner and M. R. Fenske, *Anal. Chem.*, **22**, 1074 (1950); (e) reference 11, Serial Nos. 128 and 129.

TABLE VIII

SPECTRA OF 2,3-DIMETHYL-2-BUTENE, 0–1700 CM.$^{-1}$

Raman (liquid) $\Delta\nu$, cm.$^{-1}$	I	ρ	Infrared (liquid) ν, cm.$^{-1}$	I	Assignment
Inactive fundamental, *ca.* 165 cm.$^{-1}$					Skeletal twist A_u
257	vvvw				$420 - 165 = 255\ B_{3g}$
269	vvvw		272	m	Skeletal bend. B_{2u}
			315	s	Skeletal bend. B_{1u}
411	3.1	0.50			Skeletal bend. A_g
			420	m	Skeletal bend. B_{3u}
503	4.0	0.92	*ca.* *499*	m	Skeletal bend. B_{1g} & B_{2g}
559	vvvw				$971 - 420 = 551\ B_{1g}$
			565	w	$971 - 411 = 560\ B_{2u}$
			588	m	$272 + 315 = 587\ B_{3g}$
			ca. 661	w	$165 + 503 = 668\ B_{1u}$ & B_{2u}
			670	w	
			ca. 684	w	$272 + 411 = 683\ B_{2u}$
691	8.2	0.15			C–C str. A_g
			818	w	C–C str. B_{3u}
			ca. 870	vw	$1028 - 165 = 863\ B_{1u}$
			ca. 890	vw	?
944	0.2	0.52			CH_3 rock. A_g
Unobsd. fundamental, *ca.* 961 cm.$^{-1}$					CH_3 rock. B_{3g}
			971	m	CH_3 rock. B_{2u}
1028	0.7	0.79			CH_3 rock. B_{1g}
			1065	w	CH_3 rock. B_{1u}
1072	0.8	0.68			CH_3 rock. B_{2g}
1113	vvvw				$411 + 691 = 1102\ A_g$
1132	vvvw				$315 + 818 = 1133\ B_{2g}$
			1152	m sh	C–C str. B_{2u}
			1163	s	CH_3 rock. B_{3u}
1190	vvvw				$503 + 691 = 1194\ B_{1g}$ & B_{2g}
			ca. 1210	vw	$272 + 944 = 1216\ B_{2u}$
1221	0.1				$165 + 1065 = 1230\ B_{1g}$
1269	0.2	0.78			C–C str. B_{1g}
1324	vvw				$165 + 1163 = 1328\ B_{3g}$
			1363	s	CH_3 bend., sym.
1371	0.8	0.74			
1392	3.2	0.28			
			1440	s	CH_3 bend., unsym.
1454	3.3	0.79			
			1560	w	$411 + 1152 = 1563\ B_{2u}$
1652	0.1	0.85			$691 + 961 = 1652\ B_{3g}$
			1657	w sh	$503 + 1152 = 1655\ B_{3u}$
1674	6.7	0.24			C=C str. A_g

used as those used by Kilpatrick and Pitzer[16] in similar calculations for propene and three butenes. The calculated values of the frequencies are listed in the third column of Table IX. Most of the direct assignment of fundamental frequencies from the observed spectra, as given in the fourth column of Table IX, was readily made by comparison with the calculated values and application of the selection rules. Only a few details require explanation. The calorimetric data required that the inactive A_u skeletal twisting mode have a frequency of about 165 cm.$^{-1}$ Spectroscopic confirmation of that assignment was obtained from several observed Raman lines and infrared bands that were satisfactorily explained as sum or difference combinations of observed fundamentals with an unobserved fundamental at 165 cm.$^{-1}$ The calculated values of the B_{1g} and B_{2g} skeletal bending frequencies suggested that these could be nearly coincident, and the observed Raman line at 503 cm.$^{-1}$ was used for both fundamentals. The B_{3g} methyl rocking fundamental was not observed directly. However, the Raman line at 1652 cm.$^{-1}$, for which there is no explanation in terms of observed fundamentals, can be explained as a sum combination involving the unobserved B_{3g} fundamental at about 961 cm.$^{-1}$, a value in reasonable agreement with the calculated one.

TABLE IX

CALCULATED AND OBSERVED FREQUENCIES OF 2,3-DIMETHYL-2-BUTENE V_h SYMMETRY

Class and selection rules	Motion	Calcd., cm.$^{-1}$	Obsd., cm.$^{-1}$
A_g, Raman (p)	C=C str.	1734	1674 R(p)
	CH_3 rock.	976	944 R(p)
	C–C str.	661	691 R(p)
	Skeletal bend.	298	411 R(p)
A_u, inactive	CH_3 rock.	990 or 992[a]	Not obsd
	Skeltal twist.	183 or 222[a]	165 Comb.
B_{1g}, Raman (d)	C–C str.	1482	1269 R(d)
	CH_3 rock.	974	1028 R(d)
	Skeletal bend.	473	503 R(d)
B_{2g}, Raman (d)	CH_3 rock.	1074	1072 R(?)
	Skeletal bend.	483	503 R(d)
B_{3g}, Raman (d)	CH_3 rock.	987	961 Comb.
B_{1u}, infrared	CH_3 rock.	1055	1065 I.R.
	Skeletal bend.	276	315 I.R.
B_{2u}, infrared	C–C str.	1241	1152 I.R.
	CH_3 rock.	976	971 I.R.
	Skeletal bend.	214	272 I.R.
B_{3u}, infrared	CH_3 rock.	1128	1163 I.R.
	C–C str.	868	818 I.R.
	Skeletal bend.	405	420 I.R.

[a] Depending on the assumption about the force constant for skeletal twisting.

The set of frequencies selected for thermodynamic calculations included all those listed in the fourth column of Table IX and the following: (a) the calculated value of 990 cm.$^{-1}$ for the inactive A_u methyl rocking frequency, for which no assignment could be made from the spectra; and (b) average values of 1375 (4), 1450 (8) and 2950 (12) cm.$^{-1}$ for the methyl bending and C–H stretching frequencies, which are relatively unimportant thermodynamically and for which no detailed assignment was attempted.

Moments of Inertia, Barriers to Internal Rotation and Anharmonicity.—The moments of inertia were calculated for a structure with a planar carbon skeleton and the following bond distances and angles: C=C, 1.353 Å.; C–C, 1.54 Å.; C–H, 1.09 Å.; C–C–C, 120°; C–C–H and H–C–H, 109° 28′. The calculated values are 2.097, 2.569 and 4.454 $\times 10^{-38}$ g. cm.^{2} for the principal moments of inertia, 2.399 $\times 10^{-113}$ g.^{3} cm.^{6} for their product, and 5.186 $\times 10^{-40}$ g. cm.^{2} for the reduced moment for internal rotation of each methyl group. The symmetry number for over-all rotation is 4.

Threefold, cosine-type barriers were assumed for the internal rotation of the methyl groups, and potential coupling between the different internal rotations was neglected. A barrier height of 680 cal. mole^{-1} was selected for thermodynamic calculations because it gave the best agreement with the calorimetric values of the entropy and of the heat capacity at the lower temperatures where the effect of anharmonicity is small. Such a low barrier height seems to be characteristic of methyl groups that have the *cis* configuration across a double bond, since similarly low values have been found

---

[16] J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **38**, 191 (1947).

for *cis*-2-butene[17] and for two of the methyl rotations in 2-methyl-2-butene.[18]

The contributions of anharmonicity to the thermodynamic functions were treated by the empirical method of McCullough, *et al.*[19] The two empirical constants Z = 1.17 cal. deg.$^{-1}$ mole^{-1} and ν = 1250 cm.$^{-1}$ were selected to give a satisfactory fit to the calorimetric values of the heat capacity over the whole experimental temperature range. Use of Pennington and Kobe's tables[20] simplified the numerical calculations. The calculated contributions were insignificant at the lowest temperatures and amounted to 0.2% of the free energy function, 1.3% of the heat content function, 0.5% of the entropy and 2.1% of the heat capacity at 1500°K.

Thermodynamic Functions.—The vibrational assignment and molecular-structure parameters given in the two previous sections were used to compute the functions $(F^\circ - H^\circ_0)/T$, $(H^\circ - H^\circ_0)/T$, $H^\circ - H^\circ_0$, S° and C°_p for 2,3-dimethyl-2-butene for selected temperatures up to 1500°K. These functions are tabulated in Table X. Some values in Table X are given to more decimal places than is justified by their absolute accuracy in order to retain internal consistency within the table. The satisfactory fit obtained with the calorimetric data may be judged by the comparisons of observed and calculated values of S° and C°_p in Tables VII and VI.

TABLE X

THE MOLAL THERMODYNAMIC FUNCTIONS OF 2,3-DIMETHYL-2-BUTENE

T, °K.	$(F^\circ - H^\circ_0)/T$, cal. deg.$^{-1}$	$(H^\circ - H^\circ_0)/T$, cal. deg.$^{-1}$	$H^\circ - H^\circ_0$, kcal.	S°, cal. deg.$^{-1}$	C°_p, cal. deg.$^{-1}$
273.16	− 65.59	19.04	5.200	84.63	27.71
298.16	− 67.30	19.85	5.918	87.15	29.54
300	− 67.42	19.91	5.972	87.33	29.68
400	− 73.62	23.33	9.331	96.95	37.48
500	− 79.20	26.93	13.46	106.13	45.04
600	− 84.43	30.54	18.32	114.96	51.78
700	− 89.38	34.01	23.81	123.39	57.67
800	− 94.14	37.30	29.84	131.44	62.78
900	− 98.71	40.39	36.35	139.09	67.25
1000	−103.11	43.28	43.28	146.39	71.14
1100	−107.37	45.96	50.56	153.33	74.55
1200	−111.48	48.47	58.16	159.95	77.51
1300	−115.46	50.80	66.04	166.26	80.08
1400	−119.30	52.97	74.16	172.27	82.33
1500	−123.03	54.99	82.49	178.02	84.31

Acknowledgment.—The authors wish to thank Dr. J. Rud Nielsen, of the Physics Department, University of Oklahoma, for his help in having the Raman spectrum studied in his laboratory.

BARTLESVILLE, OKLAHOMA

---

[17] J. E. Kilpatrick and K. S. Pitzer, *J. Research Natl. Bur. Standards*, **37**, 163 (1946).

[18] D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, THIS JOURNAL, **71**, 2767 (1949).

[19] J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and G. Waddington, *ibid.*, **76**, 2661 (1954).

[20] R. E. Pennington and K. A. Kobe, *J. Chem. Phys.*, **22**, 1442 (1954).

[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY]

Observations on the Addition Compound of Silicon Tetrafluoride and Ammonia

BY DONALD B. MILLER AND HARRY H. SISLER

RECEIVED MAY 18, 1955

The addition compound $SiF_4 \cdot 2NH_3$ has been prepared in a highly purified form. Its X-ray diffraction pattern has measured, as well as its dissociation pressure over the range of 351.9 to 422.4°K. Observations concerning the susceptibility of this substance to ammonolysis and hydrolysis have been made.

The preparation of a diammoniate of silicon tetrafluoride was first reported nearly a century and a half ago[1] and has been discussed in a few publications[2,3] since that time. However, the properties of the substance have not been well-defined. It became necessary, in connection with our research program, to prepare this material and to study some of its properties. We are hereby reporting some of the resulting observations. These fall under the following classifications: (a) susceptibility to hydrolysis, (b) resistance to ammonolysis, (c) vapor pressure measurements, and (d) X-ray diffraction pattern.

Preparation and Analysis.—The complex was prepared (method 1) by passing silicon tetrafluoride (prepared by treating a mixture of sodium fluosilicate and silica with concentrated sulfuric acid, and dried by passing through concentrated sulfuric acid, glass wool, phosphorus(V) oxide, and a trap cooled with Dry Ice) into a chamber containing an excess of gaseous ammonia. The complex settled out in the chamber as a fluffy, white powder.

A second method (method II) used for the preparation involved the freezing out, at liquid air temperatures, of a sample of silicon tetrafluoride, and then freezing out on top of this an excess of ammonia. The cooling bath was then removed and the mixture allowed to warm up and the excess ammonia to evaporate.

The products were analyzed for ammonia by distillation with sodium hydroxide into a 4% boric acid solution followed by titration with standard HCl soln. Fluorine and silicon determinations were made on the same sample of complex. The sample was added to water and any silicic acid which formed was filtered off and retained. Fluorine was then determined in the filtrate as lead fluorochloride.[4] The filtrate obtained upon removal of the lead fluochloride was evaporated to dryness, taken up in concentrated HCl, and the silicic acid filtered off. This was combined with the previously obtained material and ignited and weighed.

The typical product prepared by method I gave the following analytical results: Found: NH_3, 23.0, 22.8; Si, 20.8, 20.9, 21.9, 20.8; F, 55.6, 56.4, 56.1, 55.7. Calcd. for $SiF_4 \cdot 2NH_3$: NH_3, 24.7; Si, 20.3; F, 55.0. The ammonia analysis is, therefore, low. On standing with no special

---

[1] J. Davy, *Phil. Trans.*, **102**, 353 (1812).

[2] W. Mixter, *Am. Chem. J.*, **2**, 153 (1881).

[3] J. Gierut, F. Sowa and J. Nieuland, THIS JOURNAL, **58**, 786 (1936).

[4] R. Belcher and J. Tallow, *The Analyst*, **76**, 593 (1951).