Acknowledgment.—The authors are indebted to Mrs. Katherine J. Sholtz for carrying out the microbiological tests.

Experimental[12]

Guanazine Hydrobromide (III).—This compound was prepared essentially by the procedure of Pellizzari and Cantoni.[13]

3-Amino-6,7-diphenyl-*s*-triazolo-(4,3-b)-*as*-triazine (IV).—To a mixture of 5.4 g. (0.028 mole) of guanazine hydrobromide and 5.8 g. (0.028 mole) of benzil in 40 ml. of water, 40 ml. of methyl ethyl ketone and 40 ml. of ethanol was added 1.4 g. (0.035 mole) of solid sodium hydroxide. The color of the reaction mixture turned instantly to blood-red. The resulting blood-red solution was heated under reflux for 30 minutes, cooled and water added until no more solid separated. After allowing the mixture to stand for several hours, the solid was separated, washed thoroughly with water and recrystallized from absolute ethanol. The yield of bright red needles was 4.2 g. (53%), m.p. 263–264°. The analytical sample was prepared by sublimation at 240° (0.1 mm.).

Anal. Calcd. for $C_{16}H_{12}N_6$: C, 66.6; H, 4.2; N, 29.1. Found: C, 66.6; H, 4.2; N, 29.1.

3-Amino-6,7-dimethyl-*s*-triazolo(4,3-b)-*as*-triazine (V).—A solution of 15.0 g. (0.077 mole) of guanazine hydrobromide and 6.8 g. (0.079 mole) of biacetyl in 130 ml. of boiling water was adjusted to *p*H 5 by the careful addition of ammonium hydroxide. An immediate separation of beautiful yellow platelets occurred. After cooling the mixture overnight at 0°, the crystals were filtered, washed thoroughly with water and recrystallized from 95% ethanol, yield 10.47 g. (83%), m.p. 299–300°.

Anal. Calcd. for $C_6H_8N_6$: C, 43.9; H, 4.9; N, 51.2. Found: C, 44.1; H, 4.9; N, 51.2.

3-Amino-6,7-bis-(*p*-chlorophenyl)-*s*-triazolo(4,3-b)-*as*-triazine (VI).—A solution of 5.0 g. (0.018 mole) of *p,p'*-dichlorobenzil in a mixture of 80 ml. of ethyl methyl ketone and 80 ml. of ethanol was added to a solution of 3.5 g. (0.018 mole) of guanazine hydrobromide in 80 ml. of hot water, 48 g. (0.12 mole) of solid sodium hydroxide added and the blood-red solution heated under reflux for one-half hour. Addition of the cooled reaction mixture to 400 ml. of water containing 10 g. of calcium chloride resulted in the separation of a red solid, yield 4.17 g. (65%), m.p. 228–230°. Recrystallization from methylene chloride–petroleum ether raised the melting point to 229–231°.

Anal. Calcd. for $C_{16}H_{10}N_6Cl_2$: C, 53.8; H, 2.8; N, 23.5. Found: C, 53.9; H, 3.0; N, 23.9.

3-Amino-*s*-triazolo(4,3-b)phenanthro(9,10-e)-*as*-triazine (VII).—A mixture of 5.0 g. (0.024 mole) of 9,10-phenanthrenequinone, 4.7 g. (0.024 mole) of guanazine hydrobromide, 100 ml. of ethanol, 40 ml. of water and 1.7 g. (0.043 mole) of solid sodium hydroxide was heated under reflux for one-half hour. The blood-red solution was then cooled and poured into 500 ml. of water. The precipitated red solid was collected by filtration, washed with water followed by warm benzene to remove any unreacted quinone and recrystallized from glacial acetic acid to give lustrous red prisms, yield 6.63 g. (96.5%), m.p. 334–336° dec.

Anal. Calcd. for $C_{16}H_{10}N_6$: C, 67.1; H, 3.5; N, 29.4. Found: C, 67.1; H, 3.7; N, 29.3.

3-Amino-6(or 7)-methyl-7(or 6)-hydroxy-*s*-triazolo(4,3-b)-*as*-triazine (VIII).—A mixture of 5.9 g. (0.03 mole) of guanazine hydrobromide, 2.8 g. (0.032 mole) of freshly-distilled pyruvic acid and 50 ml. of 2 *N* sulfuric acid was heated under reflux for two hours and then concentrated to approximately 5 ml. Careful neutralization of the solution to *p*H 6 with 3 *N* sodium hydroxide resulted in the separation of shiny, light tan crystals which were separated by filtration and recrystallized from water, yield 2.85 g. (57%), m.p. 317–318° dec.

Anal. Calcd. for $C_5H_6N_6O$: C, 36.1; H, 3.6; N, 50.6. Found: C, 36.0; H, 3.7; N, 50.8.

3-Mercapto-6,7-diphenyl-*s*-triazolo(4,3-b)-*as*-triazine (IX).—A solution of 6.0 g. (0.046 mole) of 3,4-diamino-5-mercapto-1,2,4-triazole,[9] 9.64 g. (0.046 mole) of benzil and 1.9 g. (0.047 mole) of solid sodium hydroxide in 45 ml. of water and 75 ml. of ethanol was heated under reflux for one hour. Cooling caused the separation of red-brown crystals which were separated by filtration and washed with cold ethanol to remove unreacted benzil. The crude yield of the sodium salt of 3-mercapto-6,7-diphenyl-*as*-triazolo(4,3-b)-*as*-triazine was 13.4 g. (89%).

Glacial acetic acid was added to a suspension of 1.5 g. of the above sodium salt in 10 ml. of hot water until the solution was strongly acid. Addition of water and cooling caused the separation of 0.90 g. of an orange solid which was collected by filtration, washed with cold ethanol and extracted in a Soxhlet extractor with 50 ml. of methylene chloride. The yellow solid which separated from the extract was recrystallized from aqueous dimethylformamide to give long orange needles, yield 0.50 g. (36%), m.p. 305.4–306.6° dec.

Anal. Calcd. for $C_{16}H_{11}N_5S$: C, 62.9; H, 3.6; N, 22.9. Found: C, 63.0; H, 3.5; N, 23.1.

3-Methylmercapto-6,7-diphenyl-*s*-triazolo(4,3-b)-*as*-triazine (X).[9]—A suspension of 3.35 g. (0.01 mole) of the above sodium salt of 3-mercapto-6,7-diphenyl-*s*-triazolo(4,3-b)-*as*-triazine in 150 ml. of water was treated with 1.45 g. (0.011 mole) of methyl iodide and the mixture stirred at room temperature for three hours. The resulting yellow solid was collected by filtration and recrystallized from aqueous dimethylformamide to give 1.78 g. (55%) of yellow needles, m.p. 201–203°.

Anal. Calcd. for $C_{17}H_{13}N_5S$: C, 63.9; H, 4.1; N, 21.9. Found: C, 64.2; H, 4.0; N, 21.9.

Attempts to convert IX or X to 3-amino-6,7-diphenyl-*s*-triazolo(4,3-b)-*as*-triazine (IV) by heating with saturated alcoholic ammonia at 180° for 20 hours or by heating under reflux for 48 hours with potassium amide in toluene were unsuccessful; only unreacted starting material was isolated in each instance.

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[12] All melting points are corrected. The microanalyses were carried out by Mrs. Esther Fett, Mrs. Katherine Pih and Mr. Joseph Nemeth.

[13] G. Pellizzari and C. Cantoni, *Gazz. chim. ital.*, **35**, I, 291 (1905).

Thermodynamic Functions of Paraffins

BY GEORGE W. THOMSON

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The direct calculation of the thermodynamic functions of complex molecules by the statistical methods which have been applied to simple molecules is not possible with our present knowledge. However, a number of useful approximation methods are available. Pitzer[1] showed that the functions for *n*-paraffins and some of the simpler branched compounds could be estimated by adding the contributions for the translational and over-all rotational motion (designated F_0), the C–C stretching vibrations and the C–C bending vibrations of the skeleton, the internal rotation of the skeleton, the internal rotation and vibrations of the CH_3 groups and the vibrations of the CH_2 groups. In addition a function was included to allow for the steric interaction energy associated with different possible equilibrium positions of the rigid molecule.

These calculations were later refined and extended by Person and Pimentel[2] who re-evaluated most of the contributions using newer data. Their tables were presented for 298.16°K. and for 300 to 1500°K. at 100°K. intervals. It is the purpose of the present note to extend these tables down to 200°K., using their methods and equations, and to

[1] K. S. Pitzer, *J. Chem. Phys.*, **8**, 711 (1940).

[2] W. S. Person and G. C. Pimentel, THIS JOURNAL, **75**, 532 (1953).

TABLE I

THERMODYNAMIC FUNCTIONS FOR PARAFFINS. TERMS FOR $-(F^\circ - H_0^\circ)/T$

For $\sigma = 2$; $F(\sigma) = -1.377$.

Temp., °K.	F_0	C–C stretch	C–C bend	I_{rot} skel.	F_{steric}		CH$_3$		CH$_2$ vibr.
					A	B	I_{rot}	Vibr.	
200	46.350	0.691	0.943	2.390	3.205	0.775	0.436	0.006	0.003
220	47.107	.692	1.006	2.512	3.488	.842	.519	.010	.006
240	47.799	.695	1.069	2.629	3.739	.901	.602	.017	.010
260	48.435	.698	1.133	2.743	3.961	.954	.684	.026	.016
280	49.024	.702	1.195	2.855	4.158	1.000	.767	.037	.023
300	49.573	.708	1.257	2.961	4.335	1.041	.847	.052	.033
320	50.086	.714	1.319	3.064	4.495	1.078	.927	.069	.045
340	50.568	.721	1.379	3.164	4.638	1.111	1.006	.089	.060
360	51.022	.730	1.438	3.261	4.769	1.142	1.082	.113	.077
380	51.452	.739	1.497	3.354	4.888	1.170	1.157	.139	.096
400	51.860	.749	1.554	3.443	4.997	1.195	1.231	.169	.118
420	52.247	.761	1.610	3.530	5.097	1.218	1.303	.202	.142
440	52.617	.773	1.665	3.614	5.188	1.240	1.372	.238	.169
460	52.971	.785	1.719	3.695	5.273	1.259	1.439	.277	.198
480	53.309	.799	1.771	3.774	5.352	1.278	1.505	.318	.229
500	53.633	.813	1.823	3.849	5.425	1.295	1.570	.363	.263

TABLE II

THERMODYNAMIC FUNCTIONS FOR PARAFFINS. TERMS FOR $(H^\circ - H_0^\circ)/T$

$F(\sigma) = 0$.

Temp., °K.	F_0	C–C stretch	C–C bend	I_{rot} skel.	F_{steric}		CH$_3$		CH$_2$ vibr.
					A	B	I_{rot}	Vibr.	
200	7.949	0.013	0.632	1.225	3.020	0.714	0.826	0.037	0.021
220	7.949	.022	.697	1.315	2.927	.688	.915	.061	.037
240	7.949	.034	.759	1.394	2.825	.663	.997	.092	.059
260	7.949	.049	.819	1.463	2.720	.638	1.072	.132	.087
280	7.949	.067	.874	1.524	2.616	.614	1.142	.180	.122
300	7.949	.087	.926	1.577	2.515	.590	1.205	.236	.164
320	7.949	.110	.974	1.625	2.419	.567	1.261	.301	.212
340	7.949	.135	1.018	1.667	2.328	.546	1.316	.373	.266
360	7.949	.161	1.059	1.705	2.241	.525	1.363	.451	.326
380	7.949	.188	1.097	1.738	2.160	.505	1.406	.536	.392
400	7.949	.215	1.132	1.767	2.083	.487	1.446	.627	.462
420	7.949	.244	1.165	1.792	2.011	.470	1.483	.722	.536
440	7.949	.273	1.195	1.814	1.943	.454	1.516	.821	.614
460	7.949	.301	1.224	1.833	1.879	.439	1.546	.924	.695
480	7.949	.330	1.250	1.849	1.819	.424	1.572	1.031	.779
500	7.949	.358	1.275	1.863	1.762	.411	1.595	1.140	.865

TABLE III

THERMODYNAMIC FUNCTIONS FOR PARAFFINS. TERMS FOR S°

For $\sigma = 2$; $F(\sigma) = -1.377$.

Temp., °K.	F_0	C–C stretch	C–C bend	I_{rot} skel.	F_{steric}		CH$_3$		CH$_2$ vibr.
					A	B	I_{rot}	Vibr.	
200	54.299	0.703	1.575	3.615	6.225	1.489	1.262	0.043	0.025
220	55.056	.714	1.703	3.827	6.415	1.530	1.434	.071	.043
240	55.748	.729	1.828	4.023	6.564	1.564	1.599	.109	.069
260	56.384	.747	1.952	4.206	6.681	1.592	1.756	.158	.103
280	56.973	.769	2.069	4.379	6.774	1.614	1.909	.218	.145
300	57.522	.795	2.183	4.538	6.850	1.631	2.052	.288	.197
320	58.035	.824	2.293	4.689	6.914	1.645	2.188	.370	.257
340	58.517	.856	2.397	4.831	6.966	1.657	2.322	.462	.326
360	58.971	.891	2.497	4.966	7.010	1.667	2.445	.564	.403
380	59.401	.927	2.594	5.092	7.048	1.675	2.563	.676	.488
400	59.809	.965	2.686	5.210	7.080	1.682	2.678	.796	.580
420	60.196	1.005	2.775	5.322	7.108	1.688	2.786	.924	.678
440	60.566	1.046	2.860	5.428	7.131	1.694	2.888	1.059	.783
460	60.920	1.086	2.943	5.528	7.152	1.698	2.985	1.201	.893
480	61.258	1.129	3.021	5.623	7.171	1.702	3.077	1.349	1.008
500	61.582	1.171	3.098	5.712	7.187	1.706	3.165	1.502	1.128

present the values in Tables I to IV which are at closer intervals of temperature in order to avoid excessive interpolation errors. It is hoped that these results may be of value in thermodynamic network calculations involving hydrocarbons.

The methods used were straightforward. The

TABLE IV

THERMODYNAMIC FUNCTIONS FOR PARAFFINS. TERMS FOR C_p°

$F(\sigma) = 0.$

Temp., °K.	F_0	C–C stretch	C–C bend	I_{rot} skel.	F_{steric}		CH$_3$		CH$_2$ vibr.
					A	B	I_{rot}	Vibr.	
200	7.949	0.088	1.277	2.207	2.167	0.494	1.757	0.238	0.151
220	7.949	.138	1.400	2.242	1.836	.422	1.857	.364	.242
240	7.949	.198	1.494	2.274	1.571	.362	1.941	.520	.357
260	7.949	.265	1.567	2.301	1.356	.312	2.011	.704	.497
280	7.949	.338	1.625	2.322	1.181	.270	2.067	.913	.657
300	7.949	.413	1.672	2.336	1.037	.236	2.110	1.143	.839
320	7.949	.488	1.710	2.346	0.917	.208	2.145	1.391	1.034
340	7.949	.564	1.742	2.344	.816	.184	2.173	1.653	1.242
360	7.949	.639	1.768	2.338	.731	.165	2.192	1.924	1.458
380	7.949	.710	1.791	2.326	.658	.149	2.200	2.204	1.681
400	7.949	.779	1.810	2.309	.595	.135	2.201	2.485	1.908
420	7.949	.845	1.826	2.288	.541	.123	2.199	2.769	2.136
440	7.949	.907	1.840	2.263	.494	.112	2.189	3.053	2.365
460	7.949	.965	1.853	2.235	.452	.103	2.176	3.335	2.592
480	7.949	1.020	1.864	2.205	.415	.094	2.159	3.614	2.816
500	7.949	1.072	1.874	2.174	.382	.087	2.138	3.890	3.038

vibrational contributions were obtained by linear interpolation in the ONR Einstein function tables[3] and are estimated to be accurate to ±0.001 unit if the given frequencies are accepted. The terms for I_{rot} for the skeleton were obtained by four-point Lagrangean interpolation in the Pitzer and Gwinn[4] tables and are accurate to ±0.001 unit. However, the corresponding terms for I_{rot} for the methyl groups which were obtained in a similar fashion were not as smooth and may deviate from smoothness by ±0.003 unit. (Previous experience has indicated that the body of the Pitzer and Gwinn tables is not smooth to better than ±0.003 to 0.005 unit.)

TABLE V

THERMODYNAMIC FUNCTIONS OF *n*-HEPTANE. IDEAL GAS STATE

T, °K.	$-F^\circ - H_0^\circ/T$	$H^\circ - H_0^\circ/T$	S°	C_p°
200	67.495	20.937	88.432	30.602
210	68.527	21.416	89.944	31.403
220	69.535	21.889	91.424	32.232
230	70.519	22.357	92.876	33.092
240	71.480	22.823	94.303	33.982
250	72.421	23.288	95.709	34.901
260	73.343	23.752	97.096	35.848
270	74.248	24.218	98.467	36.821
280	75.137	24.686	99.823	37.816
290	76.001	25.156	101.167	38.834
300	76.872	25.629	102.501	39.868
310	77.720	26.105	103.825	40.915
320	78.557	26.584	105.141	41.971
330	79.383	27.066	106.449	43.033
340	80.198	27.552	107.749	44.098
350	81.003	28.040	109.043	45.164
360	81.799	28.530	110.330	46.228
370	82.588	29.023	111.611	47.287
380	83.369	29.517	112.886	48.341
390	84.142	30.013	114.155	49.386
400	84.908	30.511	115.419	50.422
410	85.668	31.009	116.676	51.446
420	86.421	31.508	117.928	52.459
430	87.168	32.007	119.174	53.459
440	87.909	32.505	120.415	54.446
450	88.646	33.003	121.650	55.418
460	89.377	33.501	122.878	56.377
470	90.102	33.998	124.100	57.321
480	90.823	34.494	125.317	58.252
490	91.540	34.988	126.528	59.170
500	92.252	35.481	127.732	60.076

The values in the A column for F_{steric} are for *n*-heptane and were computed directly; for a = 500 cal./mole they are accurate to ±0.001 unit. The B values corresponding to the CH$_2$ increment above *n*-heptane were found by calculation of the "steric" functions for *n*-octane, *n*-nonane and *n*-decane at 200 and 300°K. The increment was found to be constant to ±0.0005 unit. The values at the 20° intervals shown were computed by five-point Lagrangean interpolation. These may be uncertain by ±0.010 unit.

The thermodynamic functions for *n*-heptane presented in Table V were obtained by numerical smoothing of the results obtained by summation of the values in Tables I to IV. The smoothed values at the even 20° intervals do not differ from the direct sums by more than ±0.004, and 83% of the values differ by less than ±0.003. The values at the odd 20° intervals were obtained by three or four point Lagrangean interpolation. The table is self consistent, and the thermodynamic interrelations between the columns are satisfied.

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[3] H. L. Johnston, L. Savedoff and J. Belzer, "Contributions to the Thermodynamic Functions by a Planck–Einstein Oscillator in One Degree of Freedom," Office of Naval Research Report NAVEXOS P-646, July, 1949, Washington, D. C.

[4] K. S. Pitzer and W. D. Gwinn, *J. Chem. Phys.*, **10**, 428 (1942).

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The Action of Aluminum Chloride as a Catalyst in Alkylation Reactions

BY C. R. RAHA

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Recent communications by this author[1,2] have described the use of aluminum chloride as a catalyst in certain alkylation reactions. The present

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[1] C. Raha, THIS JOURNAL, **75**, 4098 (1953).

[2] C. Raha, *ibid.*, **75**, 4098 (1953).