[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

Heat Capacities and Dissociation Equilibria of Gases[1]

BY BERNARD LEWIS[2] AND GUENTHER VON ELBE[3]

Although accurate band spectroscopic data of heat capacities and dissociation equilibria of many gases have been made available during the past four years, we have noted that even in very recent publications the earlier approximate data are still used. In the course of our investigations on gas explosions we have gathered the above data which are available to the present time. We therefore present the following tables, which we hope will be useful to the numerous investigators in this field.

Following the custom adopted by the investigators mentioned below Lewis and Randall's system of symbols will be used.

$$E_T^\circ - E_0^\circ = \int^T C_v dT$$

The equilibrium constant K for the reaction

$$A + B \rightleftharpoons AB$$

is given by

$$K = p_A p_B / p_{AB}$$

where the partial pressures p_A, etc., are in atmospheres.

TABLE I

ENERGY CONTENT ($E_T^\circ - E_0^\circ$) OF GASES

Temp., °K.	Gas										
	H_2	O_2	N_2	CO	NO	OH	CO_2	H_2O	O_3	Br_2	HBr
200	965	995	992	992	1095	..	..	1192	1229	1134	994
250	1197	..	..	..	..	..	..	..	..	1454	1243
300	1440	1492	1489	1489	1616	1523	1660	1791	1950	1783	1493
400	1936	2004	1987	1989	2132	2034	3403	2409	2786	2456	1991
500	..	..	..	..	..	..	..	..	3660	3140	2493
600	2936	3086	3006	3017	3196	3048	4135	3687	4627	3830	3003
700	..	..	..	..	..	..	..	..	5644	4524	3525
800	3947	4262	4080	4112	4332	4069	6107	5073	6702	5222	4061
900	..	..	..	..	..	..	..	..	7793	5923	4612
1000	4979	5509	5217	5271	5534	5118	8246	6577	8909	6626	5179
1200	6044	6814	6442	6487	6786	6200	10500	8200	..	8037	6355
1400	7155	8150	7659	7749	8074	7330	12840	9920	..	9455	7579
1600	8295	9514	8920	9045	9389	8525	15220	11750	..	10880	8843
1800	9478	10920	10220	10355	10724	9740	17680	13670	..	..	..
2000	10702	12352	11533	11670	12075	10990	20180	15650	..	..	..
2200	11945	13815	12860	13007	13439	12255	22680	17710	..	..	..
2400	13233	15314	14199	14354	14814	13565	25240	19780	..	..	..
2600	14554	16825	15554	15732	16197	14890	27830	21930	..	..	..
2800	15894	18350	16926	17110	17588	16250	30450	24150	..	..	..
3000	17234	19887	18295	18484	18985	17607	33000	26330	..	..	..
3200	18586	21415	19672	19923	20387	19000	..	..	..	..	..
3500	20654	23700	21747	21951	22500	21105	..	..	..	..	..

SOURCES OF DATA

H_2: $E^\circ - E_0^\circ$; Davis and Johnston, THIS JOURNAL, **56**, 1045 (1934).

K; Giauque, *ibid.*, **52**, 4816 (1930); Davis and Johnston give slight corrections to Giauque's free energy of H_2 above 2000°. The uncertainty in ΔE_0° makes it unnecessary to consider these corrections at present.

O_2: $E^\circ - E_0^\circ$ and K; Johnston and Walker, *ibid.*, **55**, 172, 187 (1933); Lewis and von Elbe, *ibid.*, **55**, 507, 511 (1933). The values given in the tables are those of Lewis and von Elbe, which include the contribution of the oxygen $^1\Delta$ level.

N_2: $E^\circ - E_0^\circ$; Johnston and Davis, *ibid.*, **56**, 271 (1934). K; calculated from fundamental equation $R \ln K = -\Delta(F^\circ - E_0^\circ)/T - \Delta E_0^\circ/T$ using free energies of N and N_2 [Giauque and Clayton, *ibid.*, **55**, 4875 (1933)] and ΔE_0° = 168,000 cal. [Mulliken, *Phys. Rev.*, **46**, 144 (1934); also Kaplan, *ibid.*, **45**, 898 (1934); Lozier, *ibid.*, **45**, 840 (1934); Herzberg and Sponer, *Z. physik. Chem.*, **B26**, 1 (1934)].

CO: $E^\circ - E_0^\circ$; Johnston and Davis, *loc. cit.* $K_{(C + \frac{1}{2}O_2 \rightleftharpoons CO)}$; Clayton and Giauque, THIS JOURNAL, **54**, 2610 (1932); corrections are applied to their values to include the oxygen $^1\Delta$ level.

NO: $E^\circ - E_0^\circ$; Johnston and Chapman, *ibid.*, **55**, 155 (1933). $K_{(N + O \rightleftharpoons NO)}$; calculated from fundamental equation $R \ln K = -\Delta(F^\circ - E_0^\circ)/T - \Delta E_0^\circ/T$ using free energy of O (Johnston and Walker, *loc. cit.*), free energy of N (Giauque and Clayton, *loc. cit.*), free energy of NO (Johnston and Chapman, *loc. cit.*) and ΔE_0° = 121,000 cal. (Mulliken, *loc. cit.*). $K_{(NO \rightleftharpoons \frac{1}{2}O_2 + \frac{1}{2}N_2)}$; Giauque and Clayton, *loc. cit.*

H_2O: $E^\circ - E_0^\circ$; Gordon, *J. Chem. Phys.*, **2**, 65, 549 (1934). $K_{(H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O)}$; calculated from fundamental equation $R \ln K = -\Delta(F^\circ - E_0^\circ)/T - \Delta E_0^\circ/T$ using free energy of H_2 (Giauque, *loc. cit.*), free energy of O_2 (Johnston and Walker, *loc. cit.*) corrected for $^1\Delta$ level, free energy of H_2O (Gordon, *loc. cit.*) and ΔE_0° = 57,111 cal. [Rossini, *Bur. Stand. J. Res.*, **6**, 1 (1931)]. $K_{(OH + \frac{1}{2}H_2 \rightleftharpoons H_2O)}$; calculated from fundamental equation (above) using free energy of OH [Johnston and Dawson, THIS JOURNAL, **55**, 2744 (1933)], free energy of H_2 (Giauque, *loc. cit.*), free energy of H_2O (Gordon, *loc. cit.*) and ΔE_0° = 63,000 cal. [Lewis and von Elbe, *J. Chem. Phys.*, **3**, 63 (1935)].

CO_2: $E^\circ - E_0^\circ$; Kassel, THIS JOURNAL, **56**, 1838 (1934). $K_{(CO + H_2O \rightleftharpoons CO_2 + H_2)}$; calculated from fundamental equation (above) using free energy of CO (Clayton and Giauque, *loc. cit.*), free energy of H_2O (Gordon, *loc. cit.*), free energy of CO_2 (Kassel,

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TABLE II

EQUILIBRIUM CONSTANTS (LOG K) OF VARIOUS REACTIONS (ENERGIES OF REACTIONS REFER TO ABSOLUTE ZERO)

Temp., °K.	300	400	600	800	1000	1200	1400	1600	1800
$2H \rightleftharpoons H_2 + 102{,}800$	−70.9	−52.1	−32.2	−21.7	−17.19	−13.19	−10.52	− 8.48	− 6.85
$2O \rightleftharpoons O_2 + 117{,}300$	−80.2	−58.6	−36.9	−26.1	−19.48	−15.10	−11.97	− 9.61	− 7.772
$2N \rightleftharpoons N_2 + 168{,}000$	−117.2	−86.2	−55.4	−39.9	−30.6	−24.4	−19.9	−16.6	−13.9
$2Cl \rightleftharpoons Cl_2 + 56{,}900$	−36.43	−25.91	−15.32	− 9.99	− 6.77	− 4.61	− 3.06	− 1.89	− 0.977
$CO + {}^1/_2O_2 \rightleftharpoons CO_2 +$ 66,757	−44.72	−32.43	−20.07	−13.89	−10.20	−7.755	− 5.999	− 4.715	− 3.690
$H_2 + {}^1/_2O_2 \rightleftharpoons H_2O +$ 57,111	−39.77	−29.26	−18.64	−13.28	−10.05	−7.90	− 6.34	− 5.20	− 4.27
$OH + {}^1/_2H_2 \rightleftharpoons H_2O +$ 63,000	−43.3	−31.7	−20.0	−14.07	−10.53	−8.17	− 6.47	− 5.20	− 4.19
$CO + H_2O \rightleftharpoons CO_2 +$ $H_2 + 9646$	− 4.947	− 3.167	− 1.433	− 0.610	− 0.147	+0.145	+ 0.341	+ 0.485	+ 0.580
C (β-graphite) $+ {}^1/_2O_2 \rightleftharpoons$ $CO + 27{,}404$	−24.08	−19.23	−14.41	−11.98	−10.52	−9.530	− 8.817	− 8.277	− 7.850
$O_3 \rightleftharpoons 1{}^1/_2O_2 + 34{,}513$	−28.29	−22.15	−15.98	−12.89	−11.03	−9.79	− 8.89	− 8.22	− 7.70
$O_2 + O \rightleftharpoons O_3 + 24{,}137$	−11.83	− 7.16	− 2.48	− 0.13	+ 1.29	+2.24	+ 2.92	+ 3.42	+ 3.82
$NO \rightleftharpoons {}^1/_2O_2 + {}^1/_2N_2 +$ 21,400	−15.04	−11.13	− 7.194	− 5.231	− 4.052	− 3.267	− 2.706	− 2.285	− 1.959
$N + O \rightleftharpoons NO + 121{,}000$	−83.4	−61.2	−38.9	−27.7	−20.93	−16.42	−13.18	−10.76	− 8.87
${}^1/_2H_2 + {}^1/_2Cl_2 \rightleftharpoons HCl +$ 21,984	−16.57	−12.55	− 8.52	− 6.49	− 5.26	− 4.44	− 3.85	− 3.40	− 3.06
$2Br \rightleftharpoons Br_2 + 45{,}230$	−28.00	−19.61	−11.21	− 6.99	− 4.45	− 2.74	− 1.52	− 0.593	.....
${}^1/_2Br_2 + {}^1/_2H_2 \rightleftharpoons HBr +$ 11,990	− 9.37	− 7.16	− 4.93	− 3.80	− 3.11	− 2.65	− 2.32	− 2.07	.....

Temp., °K.	2000	2200	2400	2600	2800	3000	3200	3500	4000	5000
$2H \rightleftharpoons H_2 +$ 102,800	−5.53	−4.46	−3.57	−2.80	−2.13	−1.58	−1.08	− 0.434	+ 0.43	+ 1.64
$2O \rightleftharpoons O_2 +$ 117,300	−6.298	−5.091	−4.078	−3.228	−2.495	−1.858	−1.290	− 0.577	+ 0.379	+ 2.715
$2N \rightleftharpoons N_2 +$ 168,000	−11.9	−10.2	−8.72	−7.50	−6.47	−5.56	−4.77	− 3.76	− 2.39	− 0.472
$2Cl \rightleftharpoons Cl_2 +$ 56,900	−0.245	+0.356	+0.858	+1.283	+1.648	+1.965	.....	.....	.....	.....
$CO + {}^1/_2O_2 \rightleftharpoons$ $CO_2 + 66{,}757$	−2.862	−2.193	−1.648	−1.206	−0.811	−0.470	.....	.....	.....	.....
$H_2 + {}^1/_2O_2 \rightleftharpoons$ $H_2O + 57{,}111$	−3.52	−2.91	−2.41	−2.00	−1.63	−1.31	.....	.....	.....	.....
$OH + {}^1/_2H_2 \rightleftharpoons$ $H_2O + 63{,}000$	−3.40	−2.74	−2.19	−1.74	−1.34	−0.999	.....	.....	.....	.....
$CO + H_2O \rightleftharpoons CO_2 +$ $H_2 + 9646$	+0.658	+0.717	+0.762	+0.794	+0.819	+0.840	.....	.....	.....	.....
C (β-graphite) $+ {}^1/_2O_2 \rightleftharpoons$ $CO + 27{,}404$	−7.504	−7.221	−6.980	−6.777	−6.595	−6.440	.....	.....	.....	.....
$O_3 \rightleftharpoons 1{}^1/_2O_2 +$ 34,513	−7.29	−6.95	−6.66	−6.42	−6.21	−6.03	−5.87	− 5.68	− 5.40	− 5.02
$O_2 + O \rightleftharpoons O_3 +$ 24,137	+4.15	+4.41	+4.63	+4.81	+4.97	+5.11	+5.23	+ 5.39	+ 5.60	+5.89
$NO \rightleftharpoons {}^1/_2O_2 +$ ${}^1/_2N_2 + 21{,}400$	−1.695	−1.479	−1.300	−1.150	−1.019	−0.907	−0.807	− 0.680	− 0.513	− 0.279
$N + O \rightleftharpoons NO +$ 121,000	−7.35	−6.11	−5.065	−4.194	−3.431	−2.778	−2.203	− 1.465	− 0.475	+ 0.924
${}^1/_2H_2 + {}^1/_2Cl_2 \rightleftharpoons$ $HCl + 21{,}984$	−2.78	−2.55	−2.36	−2.20	−2.06	−1.94	.....	.....	.....	.....

loc. cit.; Gordon, *J. Chem. Phys.*, **1**, 308 (1933), up to 1500°K.), free energy of H_2 (Giauque, *loc. cit.*) and ΔE_0° = 9646 (from Rossini's thermal data, *Bur. Stand. J. Res.*, **6**, 37 (1931)).

$K_{(CO + {}^1/_2O_2 \rightleftharpoons CO_2)}$; calculated by multiplying $K_{(CO+H_2O \rightleftharpoons CO_2+H_2)}$ by $K_{(H_2 + {}^1/_2O_2 \rightleftharpoons H_2O)}$.

O_3: $E^\circ - E_0^\circ$; calculated from Gerhard's [*Phys. Rev.*, **42**, 622 (1932)] fundamental frequencies 528, 1033 and 1355 cm.$^{-1}$, with anharmonicity corrections, estimated by Kassel (private communication).

$K_{(O_3 \rightleftharpoons 1\frac{1}{2}O_2)}$; $K_{(O_2 + O \rightleftharpoons O_3)}$; } Kassel, *J. Chem. Phys.*, **1**, 414 (1933).

OH: $E^\circ - E_0^\circ$; Johnston and Dawson, *loc. cit.*

Cl_2: $K_{(2Cl \rightleftharpoons Cl_2)}$; $K_{(\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightleftharpoons HCl)}$; } Giauque and Overstreet, THIS JOURNAL, **54**, 1731 (1932).

Br_2: $E^\circ - E_0^\circ$ and K; HBr: $E^\circ - E_0^\circ$ and K; } Gordon and Barnes, *J. Chem. Phys.*, **1**, 693 (1933).

Summary

Accurate data of heat capacities and dissociation equilibria derived from band spectroscopic data of gases have been gathered and arranged in two tables. Table I contains the energy content of H_2, O_2, N_2, CO, NO, OH, CO_2, H_2O, O_3, Br_2 and HBr from 200 to 3500°K.; Table II contains equilibrium constants of numerous equilibria involving these gases and also Cl_2 and HCl from 300 to 5000°K. Complete references to sources of data are given.

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The Reactions Taking Place in the Iodimetric Determination of Chromates

BY FRIEDRICH L. HAHN

It has been known for a long time that in the iodimetric titration of chromates an excess of thiosulfate is often consumed.[1] This has been attributed to an air oxidation of the iodide in acid medium. However, this explanation does not account fully for the various phenomena observed in the system dichromate–acid–iodide–thiosulfate. The excess in the quantity of thiosulfate required in *feebly* acid solutions cannot be caused by the action of atmospheric oxygen, because it is large in a rapid determination, diminishes as one prolongs the titration and disappears when some time is allowed to elapse, after having acidulated the solution before beginning the titration (Kolthoff).

The author has found that the various phenomena observed can be explained by the formation of a complex between chromic chromium and thiosulfate, this complex reacting only very slowly with iodine.[2] Chromic chromium once formed does not react with the thiosulfate, but the complex is formed when the reduction of chromate takes place in the presence of thiosulfate. This hypothesis enables us to predict phenomena verifiable by experiment.

I. If the excess of reagent consumed for feebly acid solutions is not due to an excessive formation of iodine but to an irregular fixation of the thiosulfate, it must be specific for thiosulfate as reducing agent and it ought to disappear, if the liberated iodine is reduced by another reagent; this was found on titrating the iodine with stannous chloride.

II. If the excess of thiosulfate fixed into the complex reacts slowly with iodine, the theoretical quantity of iodine will be found on titrating the colorless final solution drop by drop with iodine until the iodine color is definitively stable and by subtracting this quantity of iodine from the quantity of thiosulfate consumed. This is proved by experiments.

III. The smallest traces of thiosulfate may be detected by the catalysis of a mixture of sodium azide (NaN_3) and iodine, decolorizing the iodine and forming gaseous nitrogen.[3] This reaction reveals the presence of thiosulfate in the end solutions, although containing free iodine, of titrations in which an excess of thiosulfate has been used; this thiosulfate is furnished by decomposition of the thiosulfate–chromic complex. The reaction does not take place in solutions from exact titrations.

IV. The quantity of the complex formed in a titration ought to increase with the quantity of chromate present during the addition of the thiosulfate, and this diminishes with the concentration of H^+ or I^- ions increasing. This is in agreement with the fact that the excess of thiosulfate diminishes when the acidity of the solution increases; one may anticipate that for solutions of the same concentration in acid an increase of iodide will also diminish the thiosulfate required. This also is verified by experiment (Trials a and e, b and f on Table I).

V. Regarding quantitative relations it may be anticipated that the reactions on the sodium azide

(1) G. Bruhns, *Z. anorg. allgem. Chem.*, **49**, 277 (1916); *J. prakt. Chem.*, **93**, 73, 312 (1916); **95**, 37 (1917); I. M. Kolthoff, *Z. anal. Chem.*, **59**, 401 (1920). Later investigations concerning the same subject, *e. g.*, K. and W. Böttger, *ibid.*, **69**, 145 (1926), or A. Friedrich and E. Bauer, *ibid.*, **97**, 305 (1934), have not contributed to solution of the problem in question.

(2) Preliminary publication, *Z. anal. Chem.*, **97**, 305 (1934).

(3) Reaction investigated by Fr. Feigl, *ibid.*, **76**, 376 (1928).