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Free Energy and Entropy of Translation Tables

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In the statistical caculation of the thermodynamic properties of ideal gases the translational contribution is calculated from the Sackur-Tetrode equation,

$$S = R\ln \frac{(2\pi MkT)^{3/2}}{h^3 N^{5/2}} V + 5/2\, R, \tag{1}$$

in which S is the entropy of one mole of a gas of molecular weight M, at absolute temperature T, and volume V expressed in cubic centimeters; k is Boltzmann's constant; h is Planck's constant; N is Avogadro's number; and R is the molal gas constant expressed in the same units as those desired for S, usually cal deg^{-1} $mole^{-1}$.

Separation of terms yields

$$S = \frac{3}{2} R\ln M + \frac{3}{2} R\ln T + R\ln V + R\ln \frac{(2\pi k)^{3/2}}{h^3 N^{5/2}} + \frac{5}{2} R \tag{2}$$

in which the last two terms are constants. Substitution for V from the ideal gas law gives

$$S = \frac{3}{2} R\ln M + \frac{5}{2} R\ln T - R\ln P + R\ln \frac{(2\pi k)^{3/2}}{h^3 N^{5/2}} + \frac{5}{2} R + R\ln R \tag{3}$$

in which P is the pressure of gas, usually expressed in atmospheres. The last three terms are constants but the last one requires clarification. The first R in this last term is expressed, as above, in the units desired for S, while the second one is expressed in units commensurate with the units used for V and P, usually cc-atm deg^{-1} $mole^{-1}$.

For ideal gases in their standard states, the pressure is one atm, and the entropy becomes

$$S^\circ = \frac{3}{2} R\ln M + \frac{5}{2} R\ln T + R\ln \frac{(2\pi k)^{3/2}}{h^3 N^{5/2}} + \frac{5}{2} R + R\ln R \tag{4}$$

Similarly the free energy function for translation is

$$-\frac{F^\circ - H^\circ_O}{T} = -\frac{H^\circ - TS^\circ - H^\circ_O}{T} = S^\circ - \frac{H^\circ - H^\circ_O}{T} = S^\circ - \frac{5}{2} R$$

$$= \frac{3}{2} R\ln M + \frac{5}{2} R\ln T + R\ln \frac{(2\pi k)^{3/2}}{h^3 N^{5/2}} + R\ln R \tag{5}$$

It is clear from equations (4) and (5) that the standard entropy and free energy fuction for translational motion of ideal gases depend only on the molecular weight of the gas and the temperature. To facilitate the frequently necessary calculation of these quantities, we have calculated and are presenting here the values at different temperatures of these functions apart from the molecular weight term.

Two sets of constants are currently in use: one advocated by Rossini, Johnston, Gucker, Pauling, and Vinal[1] based on the work of DuMond and Cohen[2], and one proposed in 1947 by the National Bureau of Standards in its Selected Values of Chemical Thermodynamic Properties[3]. The value for gas constant, R, is the same in both sets. Table I summarizes the values of the constants in both sets.

TABLE I

Constant	*NBS (1947)*	*R, J, G, P, and V (1952)*
R (cal deg^{-1} $mole^{-1}$)	1.98719 ± 0.00008	1.98719 ± 0.00008
R (cm^3 atm deg^{-1} $mole^{-1}$)	82 0567 ± 0.0034	82.0567 ± 0 0034
k (ergs deg^{-1} $molecule^{-1}$)	(1 38048 ± 0.00050) x 10^{-16}	(1 380257 ± 0.000067) x 10^{-16}
h (erg-sec)	(6.6242 ± 0.0044) x 10^{-27}	(6 62377 ± 0.00027) x 10^{-27}
N (molecules $mole^{-1}$)	(6.02283 ± 0.0022) x 10^{23}	(6 02380 ± 0.00016) x 10^{23}
$\frac{5}{2}$R	(4.96798 ± 0.00020)	(4 96798 ± 0 00020)
RlnR	8 75836 ± 0.00044	8 75836 ± 0.00044
$R\ln\frac{(2\pi k)^{3/2}}{h^3 N^{5/2}}$	$-16\ 0404_2$ ± 0.0045$^+$	−16 04132 ± 0.00072
$R\ln\frac{(2\pi k)^{3/2}}{h^3 N^{5/2}} + \frac{5}{2}R$	-11.0724_5 ± 0.0045$^+$	−11 07334 ± 0.00075$^-$
$R\ln\frac{(2\pi k)^{3/2}}{h^3 N^{5/2}} + \frac{5}{2}R + R\ln R$	$-2\ 3140_9$ ± 0.0045$^+$	−2 31498 ± 0.00087
$R\ln\frac{(2\pi k)^{3/2}}{h^3 N^{5/2}} + R\ln R$	$-7\ 2820_6$ ± 0.0045$^+$	−7 28296 ± 0.00084

The results of our calculations which are based on the later constants in Table I are given in Table II in which the first column gives the temperature in degrees K; the second gives the free energy function without the molecular weight term, $-\frac{F^\circ - H^\circ_0}{T} - \frac{3}{2}$ RlnM in cal deg^{-1} $mole^{-1}$; the third gives the entropy without the molecular weight term, $S^\circ - \frac{3}{2}$ RlnM in the same units; and the last gives the differences between successive entries in the two preceding columns. The additive constants in the free energy function and entropy used in the preparation of these tables are taken, as Table I indicates, to be −7.2830 and −2.3150 respectively. It is clear from the probable errors listed in

Table II. Translational Free Energy and Entropy Without Molecular Weight.

T°K	$-(F^\circ - H_0^\circ)/T$	S°	Diff.	T°K	$-(F^\circ - H_0^\circ)/T$	S°	Diff.
10	4.1562	9.1242	3.4435	2350	31.2793	36.2473	0.1045
20	7.5997	12.5677	2.0143	2400	31.3838	36.3518	0.1025
30	9.6140	14.5820	1.4293	2450	31.4863	36.4543	0.1004
40	11.0433	16.0113	1.1085	2500	31.5867	36.5547	0.0983
50	12.1518	17.1198	0.9058	2550	31.6850	36.6530	0.0965
60	13.0576	18.0256	0.7700	2600	31.7815⁻	36.7495⁻	0.0947
70	13.8276	18.7956	0.6592	2650	31.8762	36.8442	0.0928
80	14.4868	19.4548	0.5851	2700	31.9690	36.9370	0.0911
90	15.0719	20.0399	0.5235	2750	32.0601	37.0281	0.0896
100	15.5954	20.5634	2.0143	2800	32.1497	37.1177	0.0879
150	**17.6097**	**22.5777**	1.4292	2850	32.2376	37.2056	0.0864
200	19.0389	24.0069	1.1086	2900	32.3240	37.2920	0.0849
250	20.1475⁻	25.1155⁻	0.9057	2950	32.4089	37.3769	0.0835
300	21.0532	26.0212	0.7659	3000	32.4924	37.4604	0.0822
350	21.8191	26.7871	0.6633	3050	32.5746	37.5426	0.0807
400	22.4824	27.4504	0.5852	3100	32.6553	37.6233	0.0795
450	23.0676	28.0356	0.5234	3150	32.7348	37.7028	0.0783
500	23.5910	28.5590	0.4735	3200	32.8131	37.7811	0.0769
550	24.0645⁻	29.0325⁻	0.4323	3250	32.8900	37.8580	0.0759
600	24.4968	29.4648	0.3976	3300	32.9659	37.9339	0.0747
650	24.8944	29.8624	0.3682	3350	33.0406	38.0086	0.0737
700	25.2626	30.2306	0.3427	3400	33.1143	38.0823	0.0725
750	**25.6053**	**30.5733**	0.3207	3450	33.1868	38.1548	0.0715
800	**25.9260**	**30.8940**	0.3012	3500	33.2583	38.2263	0.0704
850	26.2272	31.1952	0.2839	3550	33.3287	38.2967	0.0695
900	26.5111	31.4791	0.2686	3600	33.3982	38.3662	0.0685
950	26.7797	31.7477	0.2549	3650	33.4667	38.4347	0.0676
1000	27.0346	32.0026	0.2424	3700	33.5343	38.5023	0.0667
1050	27.2770	32.2450	0.2310	3750	33.6010	38.5690	0.0658
1100	27.5080	32.4760	0.2209	3800	33.6668	38.6348	0.0649
1150	27.7289	32.6969	0.2114	3850	33.7317	38.6997	0.0641
1200	27.9403	32.9083	0.2028	3900	33.7958	38.7638	0.0634
1250	28.1431	33.1111	0.1948	3950	33.8592	38.8272	0.0624
1300	**28.3379**	33.3059	0.1875	4000	33.9216	38.8896	0.1227
1350	28.5254	33.4934	0.1808	4100	34.0443	39.0123	0.1197
1400	28.7062	33.6742	0.1743	4200	34.1640	39.1320	0.1169
1450	28.8805⁻	33.8485⁻	0.1684	4300	34.2809	39.2489	0.1142
1500	29.0489	34.0169	0.1629	4400	34.3951	39.3631	0.1116
1550	29.2118	34.1798	0.1577	4500	34.5067	39.4747	0.1093
1600	29.3695⁺	34.3375⁺	0.1528	4600	34.6160	39.5840	0.1068
1650	29.5223	34.4903	0.1484	4700	34.7228	39.6908	0.1046
1700	29.6707	34.6387	0.1440	4800	34.8274	39.7954	0.1025
1750	29.8147	34.7827	0.1399	4900	34.9299	39.8979	0.1003
1800	29.9546	34.9226	0.1362	5000	35.0302	39.9982	0.0984
1850	30.0908	35.0588	0.1324	5100	35.1286	40.0966	0.0964
1900	30.2232	35.1912	0.1291	5200	35.2250	40.1930	0.0947
1950	30.3523	35.3203	0.1258	5300	35.3197	40.2877	0.0926
2000	30.4781	35.4461	0.1226	5400	35.4125⁺	40.3805⁺	0.0912
2050	30.6007	35.5687	0.1198	5500	35.5037	40.4717	0.0895
2100	30.7205⁻	35.6885⁻	0.1169	5600	35.5932	40.5612	0.0879
2150	30.8374	35.8054	0.1142	5700	35.6811	40.6491	0.0865
2200	30.9516	35.9196	0.1116	5800	35.7676	40.7356	0.0849
2250	31.0632	36.0312	0.1093	5900	35.8525⁻	40.8205⁻	0.0835
2300	31.1725⁻	36.1405⁻	0.1068	6000	35.9360	40.9040	

Table I that the values should have an accuracy slightly better than one unit in the third decimal place.

The free energy function and entropy of translation without the molecular weight term for 298.16°K. (25°C.) are 21.0227 and 25.9907, respectively.

To obtain from the tables presented here values consistent with the NBS publications in which the additive constants have been taken as −7.2820 and −2.3141, all the values in the second column should be increased by ten in the fourth decimal and all the values in the third column should be increased by nine in the fourth decimal. To be sure,

little significance can be attached to this correction because of the large probable errors associated with the older constants.

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2. DUMOND, J. W. M. and COHEN, E. R.; *Phys. Rev.* 82 555 (1951).
3. Selected Values of Chemical Thermodynamic Properties NBS Circ. **500**, Feb. 1, 1952, and loose leaf edition Dec. 31, 1947.