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THERMODYNAMIC FUNCTIONS OF T. N. T.

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The problem of calculating thermodynamic functions of a high explosive is really the problem of evaluating them for the complex assembly of product gases, (for an explosive is no longer an explosive beyond a temperature of about 500°C[1]) given by the explosive on explosion or detonation. In view of the fact that the product gases have pressures and temperatures of the order of 10^5 atmospheres and 10^4 °K respectively, an appropriate equation of sate has to be used for the calculations. In this paper the following equation of state in the virial form, as used by Jones[2], has been employed—

$$\frac{pV'}{N'} = RT + bp + cp^2 + dp^3$$

where V′ and N′ are the volume and number of moles of the product gases ; b, and d are the virial coefficients, which are functions of temperature and of gas composition. In the present calculations however they have been assumed to be constants *i.e.* independent of temperature and the same for all gases. Their values which have been determined by comparison with experimental data, on detonation velocity versus loading density are[2]—

$$b = 25 \cdot 4,\ c = -0 \cdot 104,\ d = 2 \cdot 33 \times 10^{-4}$$

p being in units of 1000 Kg./cm². The composition of the products at $15 \cdot 9 \times 10^{10}$ dynes/cm² and 3400 °K, pressure and temperature respectively in the detonation wave front ot TNT, has been found out by Jones[2], assuming chemical and thermal equilibrium. The number of gm. moles of different products are—

$$N_{H_2} = 0 \cdot 0035,\quad N_{CO} = 0626,\quad N_{N_2} = 1 \cdot 50,\quad N_{H_2O} = 1 \cdot 10$$

$$N_{CH_4} = 0 \cdot 70,\ N_{CO_2} = 2 \cdot 45,\ N_C \text{ (Solid carbon—assumed } \beta\text{graphite)} = 3 \cdot 90.$$

This gives $N' = 5 \cdot 82$. The value of N′ as also the gas composition changes, as products expand, till the equilibrium is frozen, and the assembly acquires a constant composition. But here both N′ and gas composition have been taken to be constant throughout.

Thermal energy E is the sum of two parts E_p and E_1, E_p being the energy of gases if they were all perfect, and E_1, the correction due to imperfections at high pressures, and at these pressures E_1 is mainly due to the forces to repulsion between the molecules. Assuming Ep to be a linear function of T, its value above that at room temperature, for the detonation products of TNT in K. cal/mole of TNT is given by the expression $E_p = 0\cdot0875T - 26\cdot25$

E_1 is given by—$E_1 = -(\frac{1}{2}cp^2 + \frac{2}{3}dp^3)$ / mole of the mixture, so that

$$E = 0\cdot0875 \quad T - 26\cdot25 - 5\cdot82 \quad 1/2\ cp^2 + dp^3)$$

By irtegrating the equation

$$dH = \left(\frac{\partial H}{\partial d}\right)_T dp) + \left(\frac{\partial H}{T}\right)_p dT$$

with the help of the equation of state, the total heat H_{TP} in K.c als. at any temperature and pressure, above T=300°K, p=1 atmosphere, is given by the expression

$H_{TP} = (Ep + 5\cdot82RT) + 5\cdot82(bp + \frac{1}{2}\ cp2 + \frac{1}{3}dp3) - 3\cdot492$

In a similar way the equatior

$$ds = \left(\frac{\partial S}{cp}\right)_T dp + \left(\frac{\partial S}{\partial T}\right)_p dT$$

gives an integration, the value of the antropy, above that at room conditions, in K. cals./degree/mole of TNT.

$S_{Tp} = -RN' \log p + 0\cdot0991 \log T - 0\cdot5865$

Other functions are simple well known combinations of these—the work function F=(E—TS) and Gibbs free energy G=(H—TS).

THERMAL ENERGY E IN kil. cals./gm. mol. OF TNT.

P 1000 Kg/cm2 \ T°K	4000	3500	3000	2500	2000	1800	1600	1400	1200	1000	800	600	300
200	437·2	393·4	349·7	305·9	262·2	244·7	226·8	209·7	192·2	174·7	157·2	139·7	113·4
180	429·1	385·4	341·6	297·8	254·1	236·6	219·1	201·6	184·1	166·6	149·1	131·7	105·3
160	417·4	373·7	329·9	286·2	242·4	224·9	207·4	189·9	172·4	154·9	137·4	119·9	93·67
140	403·8	360·0	316·3	272·5	228·8	211·3	193·8	176·3	158·8	141·3	123·8	106·3	80·04
120	388·6	344·9	301·1	257·4	213·6	196·1	178·6	161·1	143·6	126·1	108·6	91·11	64·86
100	373·0	329·2	285·5	241·7	198·0	180·5	163·0	145·5	128·0	110·5	93·97	75·47	49·22
90	365·3	321·6	277·8	234·1	190·3	172·8	155·3	137·8	120·3	103·8	85·32	67·84	41·57
80	357·9	314·2	270·4	226·7	182·9	165·4	147·9	130·4	112·9	95·41	77·81	60·41	34·16
70	351·0	307·2	263·5	219·7	176·0	158·6	141·0	123·5	106·0	88·45	70·95	53·45	27·20
60	344·5	300·8	257·0	213·3	169·5	152·0	134·5	117·0	99·51	82·01	64·51	47·01	20·76
50	339·2	295·4	251·7	207·9	164·2	146·7	129·2	111·7	94·17	76·67	59·17	41·67	15·42
40	333·6	289·9	246·1	202·4	158·6	141·1	123·6	106·1	88·64	71·14	52·64	36·14	9·89
30	329·7	285·9	242·2	198·4	154·7	137·2	119·7	102·2	84·69	67·19	49·69	32·19	5·94
20	326·4	282·7	238·9	195·2	151·4	133·9	116·4	98·90	81·40	63·90	46·50	28·90	2·65
10	324·4	280·7	236·9	193·2	149·4	131·9	114·4	96·94	79·44	61·94	44·44	26·94	0·690

TOTAL HEAT H IN kil. cals./gm. mol. OF TNT.

T°K / P 1000 Kg/cm²	4000	3500	3000	2500	2000	1800	1600	1400	1200	1000	800	600	300
200	859·2	809·6	760·1	710·5	661·0	641·1	621·3	601·5	581·7	561·9	542·0	522·2	492·5
180	820·9	771·4	721·8	672·3	622·7	602·9	583·1	563·2	543·4	523·6	503·8	484·0	454·2
160	781·6	732·1	682·5	633·0	583·4	563·6	543·8	523·9	504·1	484·3	464·5	444·7	414·9
140	740·7	691·1	641·6	592·0	542·5	522·6	502·8	483·0	463·2	443·4	423·5	403·7	374·0
120	697·6	648·0	598·5	548·9	499·4	479·5	459·7	439·9	420·1	400·3	380·4	360·6	330·9
100	652·0	602·4	552·9	503·3	453·8	434·0	414·2	394·3	374·5	354·7	334·9	315·1	285·3
90	627·9	578·4	528·8	479·3	429·7	409·9	390·1	370·3	350·4	330·6	310·8	291·0	261·3
80	603·2	553·6	504·1	454·5	405·0	385·1	365·3	345·5	325·7	305·9	286·0	266·2	236·5
70	577·5	527·9	478·4	428·8	379·3	359·4	339·6	319·8	300·0	280·2	260·3	240·5	210·8
60	550·8	501·3	451·7	402·2	352·6	332·8	313·0	293·1	273·3	253·6	233·7	213·9	184·1
50	523·1	473·5	424·0	374·2	324·9	305·0	285·2	265·4	245·6	225·8	205·9	186·1	156·4
40	494·2	444·7	395·1	345·6	296·0	276·2	256·4	236·5	216·7	196·9	177·1	157·3	127·5
30	64·2	414·7	365·1	315·6	266·0	246·2	226·4	206·6	186·7	166·9	147·1	123·3	97·55
20	433·0	383·4	333·9	284·3	234·8	215·0	195·1	175·3	155·5	135·7	115·9	96·03	66·31
10	400·5	351·0	301·4	251·9	202·3	182·5	162·7	142·9	123·0	103·2	83·39	63·57	33·85

ENTROPY S IN kil. cals./degree/gm. mol. OF TNT.

P 1000 kg/cm² \ T°K	4000	3500	3000	2500	2000	1800	1600	1400	1200	1000	800	600	300
200	0·2324	0·2192	0·2036	0·1857	0·1637	0·1533	0·1416	0·1283	0·1130	0·0950	0·0729	0·0443	—0·0243
180	0·2326	0·2195	0·2038	0·1859	0·1639	0·1535	0·1418	0·1285	0·1132	0·0952	0·0731	0·0445	—0·0241
160	0·2329	0·2198	0·2041	0·1862	0·1642	0·1538	0·1421	0·1288	0·1135	0·0955	0·0734	0·0448	—0·0238
140	0·2331	0·2200	0·2043	0·1864	0·1644	0·1540	0·1423	0·1290	0·1137	0·0957	0·0736	0·0450	—0·0236
120	0·2334	0·2203	0·2046	0·1867	0·1647	0·1543	0·1426	0·1293	0·1140	0·0960	0·0739	0·0453	—0·0233
100	0·2338	0·2207	0·2050	0·1871	0·1651	0·1547	0·1430	0·1297	0·1144	0·0964	0·0743	0·0457	—0·0229
90	0·2340	0·2215	0·2052	0·1873	0·1653	0·1549	0·1432	0·1299	0·1146	0·0966	0·0745	0·0459	—0·0227
80	0·2341	0·2216	0·2053	0·1874	0·1654	0·1550	0·1433	0·1300	0·1147	0·0967	0·0746	0·0460	—0·0226
70	0·2343	0·2218	0·2055	0·1876	0·1656	0·1552	0·1435	0·1302	0·1149	0·0969	0·0748	0·0462	—0·0224
60	0·2348	0·2223	0·2062	0·1881	0·1661	0·1557	0·1440	0·1307	0·1154	0·0974	0·0753	0·0467	—0·0219
50	0·2352	0·2227	0·2066	0·1885	0·1665	0·1561	0·1444	0·1311	0·1158	0·0978	0·0757	0·0471	—0·0215
40	0·2356	0·2231	0·2070	0·1889	0·1669	0·1565	0·1448	0·1315	0·1162	0·0982	0·0761	0·0475	—0·0211
30	0·2362	0·2237	0·2076	0·1895	0·1675	0·1571	0·1454	0·1321	0·1168	0·0988	0·0767	0·0481	—0·0205
20	0·2370	0·2245	0·2084	0·1903	0·1683	0·1579	0·1462	0·1329	0·1176	0·0996	0·0775	0·0489	—0·0197
10	0·2389	0·2264	0·2103	0·1922	0·1702	0·1598	0·1481	0·1348	0·1185	0·1051	0·0794	0·0508	—0·0178

WORK FUNCTION F IN kil. cals./gm. mol. OF TNT.

P 1000 Kg/cm² \ T°K	4000	3500	3000	2500	2000	1800	1600	1400	1200	1000	800	600	300
200	—492·4	—373·8	—261·1	—158·4	—65·20	—31·24	—0·240	—30·08	+56·60	+79·70	+98·88	+113·1	+120·7
180	—503·2	—382·9	—269·8	—167·0	—73·70	—39·70	—7·780	+21·70	+48·26	+71·40	+90·62	+105·0	+112·5
160	—514·2	—395·6	—282·4	—179·3	—86·00	—51·94	—19·96	+8·580	+36·20	+59·40	+78·68	+93·02	+100·7
140	—528·6	—410·0	—296·6	—193·5	—100·0	—65·90	—31·88	—4·300	+22·36	+45·60	+64·92	+79·30	+87·08
120	—545·0	—426·2	—312·0	—209·4	—115·8	—81·64	—49·56	—19·92	+6·800	+30·10	+49·48	+63·93	+71·85
100	—562·2	—443·3	—329·5	—226·1	—132·2	—97·96	—65·80	—36·08	—9·280	+14·10	+34·53	+48·05	+56·10
90	—570·9	—453·7	—337·8	—234·2	—140·3	—106·0	—73·82	—44·06	—17·22	+7·20	+25·72	+40·30	+48·38
80	—576·5	—461·4	—345·5	—241·8	—147·9	—113·6	—81·38	—51·60	—24·74	—1·30	+18·13	+32·81	+40·94
70	—586·2	—469·1	—353·0	—249·3	—155·2	—120·8	—88·60	—58·78	—31·88	—8·450	+11·11	+25·73	+33·92
60	—594·7	—477·3	—361·6	—257·0	—162·7	—128·3	—95·90	—65·98	—38·97	—15·39	+4·270	+18·99	+27·33
50	—601·6	—484·1	—368·1	—263·4	—168·8	—134·3	—101·8	—71·84	—44·79	—21·13	—1·390	+13·41	+21·97
40	—608·8	—491·0	—374·9	—269·9	—175·2	—140·6	—108·1	—78·00	—50·80	—27·06	—8·240	+7·640	+16·22
30	—615·1	—497·1	—380·6	—275·4	—180·3	—145·6	—112·9	—82·74	—55·47	—31·61	—11·67	+3·330	+12·09
20	—621·6	—503·1	—386·3	—280·6	—185·2	—150·2	—117·5	—87·16	—59·72	—35·70	—15·50	—0·440	+8·560
10	—642·9	—511·7	—394·0	—287·3	—191·0	—155·7	—122·6	—91·82	—62·76	—39·60	—19·08	—3·540	+6·030

GIBBS FREE ENERGY IN kil. cals./gm. mol. OF TNT.

P 1000 Kg/cm² \ T°K	4000	3500	3000	2500	2000	1800	1600	1400	1200	1000	800	600	300
200	—70·40	+42·40	+149·3	+246·2	+333·6	+365·2	+394·7	+421·9	+446·1	+466·9	+483·7	+495·6	+499·8
180	—109·5	+3·150	+110·4	+207·6	+294·9	+326·6	+356·2	+383·3	+407·6	+428·4	+445·3	+457·3	+461·3
160	—150·0	—37·20	+70·20	+167·5	+225·0	+286·8	+316·4	+343·6	+367·9	+388·8	+405·8	+417·8	+422·0
140	—191·7	+78·90	+28·70	+126·0	+213·7	+245·4	+295·1	+302·4	+326·8	+347·7	+364·6	+376·7	+381·1
120	—236·0	—123·1	—15·30	+82·20	+170·0	+201·8	+231·5	+258·9	+283·3	+304·3	+322·3	+333·4	+337·9
100	—283·2	—170·1	—62·10	+35·55	+123·2	+155·5	+185·4	+21·27	+237·2	+258·3	+275·5	+287·7	+292·2
90	—308·3	—196·9	—86·80	+11·05	+99·50	+131·1	+170·9	+188·4	+212·9	+234·0	+251·2	+263·5	+268·1
80	—333·2	—222·0	—111·8	—14·00	+74·20	+106·1	+136·0	+163·5	+188·1	+209·2	+226·3	+238·6	+243·3
70	—359·7	—248·4	—138·1	—40·20	+48·10	+80·04	+110·0	+137·5	+162·1	+183·3	+200·5	+212·8	+217·5
60	—388·4	—276·8	—166·9	—68·05	+20·40	+52·54	+82·60	+110·0	+144·8	+156·2	+173·5	+185·9	+190·7
50	—417·7	—306·0	—195·8	—97·05	—8·10	+24·02	+54·16	+81·86	+106·4	+128·0	+145·3	+157·8	+162·9
40	—448·2	—336·2	—225·9	—126·7	—37·80	—5·50	+24·72	+52·40	+77·26	+98·70	+116·2	+128·8	+133·8
30	—480·6	—368·3	—257·7	—158·2	—69·00	—36·58	—6·240	+21·66	+46·54	+68·10	+85·74	+98·44	+103·7
20	—515·0	—402·4	—291·3	—160·2	—101·8	—69·22	—38·82	—10·76	+14·38	+36·10	+53·90	+66·69	+72·22
10	—555·1	—441·4	—329·5	—179·1	—138·1	—105·1	—74·26	—45·82	—19·20	—1·700	+19·87	+33·09	+39

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