

Diamond-Graphite Equilibria

The formation of diamond from graphite is simply a phase transformation given by

$$C_{\text{graphite}} = C_{\text{diamond}} \quad (1)$$

At atmospheric pressures the Gibb's energy change for the reaction is greater than zero at all temperatures. That is, graphite is the stable phase at all temperatures at atmospheric pressure. However, since diamond is the more dense form, one would expect an increase in pressure to make the formation of diamond increasingly likely. Were the pressure increased enough, the reaction should, in fact, come into equilibrium. This equilibrium is achieved between the two phases when the Gibb's energy change for the reaction at any temperature T and pressure P is zero.

A precise expression for this Gibb's energy change, $\Delta G_{P,T}^{\circ}$, is given by the equation

$$\Delta G_{P,T}^{\circ} - \Delta G_{1,T}^{\circ} = \int_1^P \Delta V_R dP \quad (2)$$

where $\Delta G_{1,T}^{\circ}$ is the Gibbs energy change at a pressure of 1 bar and temperature T.

At high pressures and temperatures the volume change is a function of both T and P and cannot be assumed constant. Consequently, an expression for the volume change is needed to complete the integration of Eq. (2). The first step in determining such an expression is to obtain an expression for the volume change of one component. The starting point is to say that the volume of a particular component is a function of T and P.

$$V = f(T,P) \quad (3)$$

The total differential is

$$dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP. \quad (4)$$

The partials may be replaced by the thermal coefficient of expansion

$$\alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (5)$$

and the isothermal coefficient of compression

$$\beta \equiv -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (6)$$

to give

$$dV = \alpha V dT - \beta V dP. \quad (7)$$

Rearranging and integrating yields

$$V = V^0 e^{\alpha \Delta T - \beta \Delta P} \quad (8)$$

which may be approximated with a McLaurin series as

$$V = V^0 (1 + \alpha \Delta T)(1 - \beta \Delta P) \quad (9)$$

This equation describes the volume of one component as a function of T and P. Noting that $\Delta P \approx P$, the volume change for reaction (1) is then

$$\Delta V_R = \Delta V_R^0 + (V_d^0 \alpha_d - V_g^0 \alpha_g) \Delta T - (V_d^0 \beta_d - V_g^0 \beta_g) P - (V_d^0 \alpha_d \beta_d - V_g^0 \alpha_g \beta_g) P \Delta T. \quad (10)$$

Substituting the numerical values from Table 1 into Eq. (10) gives

$$\Delta V_R = -(1.8811 + 115.114 * 10^{-6} \Delta T) - (15.211 * 10^{-6} + 445.80 * 10^{-12} \Delta T) P \frac{\text{cm}^3}{\text{gmole}} \quad (11)$$

where P is in units of bars. Substitution of this result into Eq. (2) and converting the units to cal/gmole gives

$$\Delta G_{P,T}^0 - \Delta G_{1,T}^0 = -(0.0450 + 2.75 * 10^{-6} \Delta T) P - (0.182 * 10^{-6} + 5.33 * 10^{-12} \Delta T) P^2 \quad (12)$$

where P is in bars.

Table 1. Data For Graphite To Diamond

	$V^0_{1,298}$ cm ³ /gmole	$S^0_{1,298}$ cal/K/gmole	α K ⁻¹	β bar ⁻¹	$\Delta G^0_f, 1,298$ cal/gmole
Diamond	3.417	0.566	10.5x10 ⁻⁶	2.0x10 ⁻⁷	693
Graphite	5.298	1.372	28.5x10 ⁻⁶	3.0x10 ⁻⁶	0

Table 2 shows a spreadsheet calculation of $\Delta G_{P,T}^0$ as a function of T and P. As can be seen, the value of $\Delta G_{P,T}^0$ declines as P goes up. At

Table 2. $\Delta G_{P,T}^{\circ}$ for Graphite to Diamond, (cal/gmole)

P, Kbars	T, K						
	298	500	1000	1500	2000	2500	3000
65	-1461	-1330	-1005	-680	-355	-31	294
64	-1440	-1308	-982	-656	-330	-4	321
63	-1418	-1286	-959	-632	-305	22	349
62	-1396	-1263	-935	-607	-279	49	377
61	-1373	-1240	-911	-582	-253	76	405
60	-1350	-1217	-887	-557	-227	104	434
59	-1327	-1193	-862	-531	-200	132	463
58	-1303	-1169	-837	-504	-172	160	492
57	-1279	-1144	-811	-478	-145	189	522
56	-1255	-1120	-785	-451	-117	218	552
55	-1230	-1094	-759	-423	-88	247	583
54	-1205	-1069	-732	-396	-59	277	614
53	-1179	-1043	-705	-368	-30	308	645
52	-1153	-1017	-678	-339	0	338	677
51	-1127	-990	-650	-310	30	369	709
50	-1101	-963	-622	-281	60	401	742
49	-1074	-935	-593	-251	91	433	775
48	-1046	-908	-564	-221	122	465	808
47	-1019	-879	-535	-191	153	498	842
46	-990	-851	-506	-160	185	531	876
45	-962	-822	-476	-129	217	564	911
44	-933	-793	-445	-98	250	598	945
43	-904	-763	-414	-66	283	632	981
42	-875	-733	-383	-33	317	667	1016
41	-845	-703	-352	-1	350	701	1053
40	-815	-672	-320	32	385	737	1089
39	-784	-641	-288	66	419	773	1126
38	-753	-610	-255	99	454	809	1163
37	-722	-578	-222	134	489	845	1201
36	-690	-546	-189	168	525	882	1239
35	-658	-513	-155	203	561	919	1277
34	-625	-480	-121	238	598	957	1316
33	-593	-447	-87	274	635	995	1356
32	-560	-413	-52	310	672	1033	1395
31	-526	-379	-17	346	709	1072	1435
30	-492	-345	19	383	747	1112	1476
29	-458	-310	55	420	786	1151	1516
28	-423	-275	91	458	825	1191	1558
27	-388	-240	128	496	864	1231	1599
26	-353	-204	165	534	903	1272	1641
25	-317	-168	202	573	943	1313	1684
24	-281	-131	240	612	983	1355	1726
23	-245	-94	278	651	1024	1397	1770
22	-208	-57	317	691	1065	1439	1813
21	-171	-19	356	731	1107	1482	1857
20	-133	19	395	772	1148	1525	1901
19	-96	57	435	813	1191	1568	1946
18	-57	96	475	854	1233	1612	1991
17	-19	135	515	896	1276	1656	2037
16	20	174	556	938	1319	1701	2083
15	59	214	597	980	1363	1746	2129
14	99	254	639	1023	1407	1792	2176
13	139	295	681	1066	1452	1837	2223
12	180	336	723	1110	1497	1883	2270
11	220	377	765	1154	1542	1930	2318
10	262	419	808	1198	1587	1977	2367
0.001	693	856	1259	1662	2065	2468	2871

298 K the phases are in equilibrium between 16 and 17 Kbars. The exact quadratic solution of Eq. (12) gives the results shown in Figure 1.

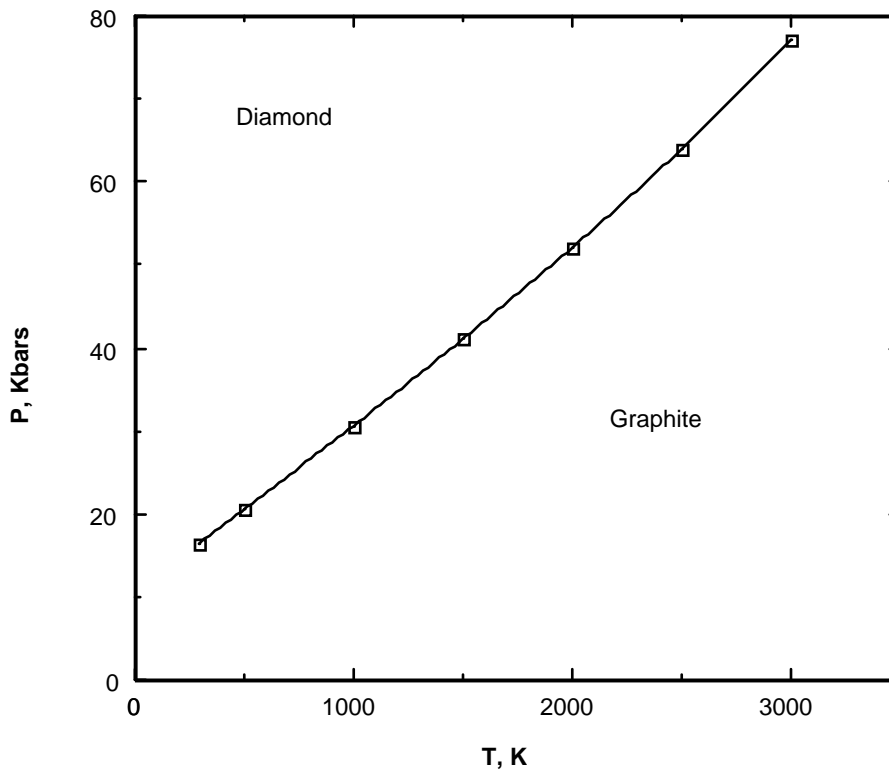


Figure 1. Phase Equilibria in the Graphite-Diamond System

Reference

Ian S. E. Carmichael, Francis J. Turner, and John Verhoogen; *Igneous Petrology*; (New York; McGraw Hill, 1974), pp. 98 -103.

Conversion factors and constants

$R=1.987 \text{ cal/K/gmole}$

1 atm = 1.013 bar