ON ENANTIOTROPY AND MONOTROPY. II.

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The behaviours of dimorphism at constant pressure may be classified at least into three categories. The first is the case in which the transition occurs in the reversible manners or enantiotropy. The second is the case in which the transition is limited in one direction or monotropy. For the third we are able to consider a case in which the transition can not occur. In the preceeding paper(1) the typical thermodynamic relations for enantiotropy and monotropy were discussed in general and it was tried to supplement the studies in this field. In the present paper these relations will be discussed for the individual cases, especially in the case of monotropy.

The Thermodynamic Eormulae Concerning the Affinity of Transition. As for the unit mass of the substance in one component, we have the following relations concerning the $\chi-$ and $\zeta-$ functions of Gibbs,

$$\left(\frac{\partial \chi}{\partial T}\right)_p = c_p,$$

$$\zeta = \chi - Ts = \chi + T\left(\frac{\partial \zeta}{\partial T}\right)_p.$$

$$\left(\frac{\partial \zeta}{\partial T}\right)_p = -s \quad \text{and} \quad \left(\frac{\partial \zeta}{\partial p}\right)_T = v\,,$$

where s, v, c_p, are the entropy, the volume and the heat capacity at constant pressure respectively concerning unit mass, p and T being pressure and absolute temperature. As the diffeence of these quantities are always necessary, the difference of these functions as the result of a virtual transition at p and T, between the two modifications, $A \rightarrow B$ will be denoted by the corresponding large letters as follows, $Z=\zeta_B-\zeta_A$, $X=\chi_B-\chi_A$, $S=s_B-s_A$, $V=v_B-v_A$ and $C_p=c_{pB}-c_{pA}$, where X is the calorimetric heat of transition expressed after the manners of Berthelot and Thomsen and Z is often called the affinity of transition respectively concerning the transition $B \rightarrow A$.

It is evident that we have the following relations among these quantities,

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(1) This journal, **3** (1928), 91.

$$\left(\frac{\partial X}{\partial T}\right)_p = C_p \qquad \text{(Kirchhoff's law)}$$

or

$$X = X_0 + \int_0^T C_p dT \qquad \cdots\cdots\cdots\cdots\cdots\cdots (1)$$

and

$$Z = X + T\left(\frac{\partial Z}{\partial T}\right)_p \qquad \text{(Gibbs and Helmholtz's law)}$$

or

$$d\left(\frac{Z}{T}\right)_p = -\frac{X}{T^2} \ .$$

By the integration of the above equation at constant pressure, we have

$$\frac{Z}{T} = \frac{Z_{T_1}}{T_1} - \int_{T_1}^T \frac{X}{T^2} dT \, . \qquad \cdots\cdots\cdots\cdots\cdots (2)$$

If we let the transition temperature be T_0 ($\neq 0$), we have

$$Z = -T \int_{T_0}^T \frac{X}{T^2} dT \, . \qquad \cdots\cdots\cdots\cdots\cdots (2a)$$

If we assume after Nernst that

$$\lim_{T=0}\left(-\frac{\partial Z}{\partial T}\right)_p = \lim_{T=0} S = o$$

or

$$S = \int_0^T \frac{C_p}{T} dT \, ,$$

we have the following relations at constant pressure,

$$\begin{aligned} Z &= Z_0 - \int_0^T S\, dT \qquad \left(\because \ \left(\frac{\partial Z}{\partial T}\right)_p = -S\right) \\ &= Z_0 - \int_0^T dT \int_0^T \frac{C_p}{T} dT \\ &= Z_0 - T\int_0^T \frac{dT}{T^2} \int_0^T C_p \, dT \\ &= X_0 - T\int_0^T \frac{X - X_0}{T^2} \, dT \, . \qquad \cdots\cdots\cdots\cdots\cdots\cdots (3) \end{aligned}$$

And we have $\left(\dfrac{\partial Z}{\partial p}\right)_T = V$.

By the integration at constant temperature, we have

$$Z = Z_{p_1} + \int_{p_1}^p V \, dp \, . \qquad \cdots\cdots\cdots\cdots\cdots\cdots (4)$$

The formulae (2) and (2a) show that we can estimate the affinity of transition within the range of temperature for which the specific heats of the two modifications are known, the affinity and the heat of transition being observed at any temperature within it. On the other hand, the formula (3) shows that we are able to estimate the affinity of transition from absolute zero to any temperature if we know the specific heats for the corresponding range of temperature and the heat of transition at any temperature within it

Evaluation of the Affinity of Transition. From the thermodynamic standpoint, the most thoroughly studied examples can be found in the dimorphism of sulphur[1] and tin.[2] In the former case, the affinity of transition was estimated on the basis of the Nernst's theorem or by the formula (3). In the latter case, it was evaluated by the formula (2a) or on the basis of the second law of thermodynamics, from the transition temperature down to absolute zero. As the result of which the Nernst's theorem was verified. These are the typical cases of enantiotropy and the Z-curves (or affinity curves) are as in the Fig. 4 in the preceeding paper. In these cases the transition point is fairly clear and the affinity of transition may also be estimated directly by the measurement of solubility[3] or e.m.f.,[4] although the range of temperature is narrowly limited. Therefore, it is able to estimate the affinity of transition within a wide range of temperature on the mere basis of the second law of thermodynamics.

In the case of diamond and graphite, however, so far as the experiments are concerned, it is almost impossible to measure the affinity of transition directly. This system was first studied by Roozeboom[5] from the standpoint of phase theory and was ascribed to the category of pseudomonotropy, although its theoretical ground is not very accurate. It seems interesting to treat it on the basis of the Nernst's theorem, for by the sole means of which we are able to evaluate the affinity of transition quantitatively. Roth[6] observed the heat of transition as follows,

$$\text{Diamond} = \text{Graphite} + 156 \text{ cal./gr. atom.} \quad (\text{at } 290°\text{K.})$$

As for the specific heats of diamond and graphite, the Nernst's[7] data have been taken for the lower temperatures and the Magnus'[8] data for the higher temperatures from 300°K. to 1100°K. The values of the heat of transition have been calculated by means of the formula (1) from 0°K to 1100°K. Next, the values of the affinity of transition have been calculated by the formula (3). In the above calculations, the Debye's T^3 law has been applied for the

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(1) W. Nernst, "Grundlagen des neuen Wärmesatzes" (1918), p. 87.

(2) J. N. Brönsted, *Z. physik. Chem.*, **88** (1914), 479. cf. F. Lange, ibid, **110** (1924) 343.

(3) J. N. Brönsted, ibid., **56** (1906), 645.

(4) E. Cohen, ibid., **30** (1899), 614.

(5) H. W. B. Roozeboom, "Die heterogenen Gleichgewichte" (1901), p. 179.

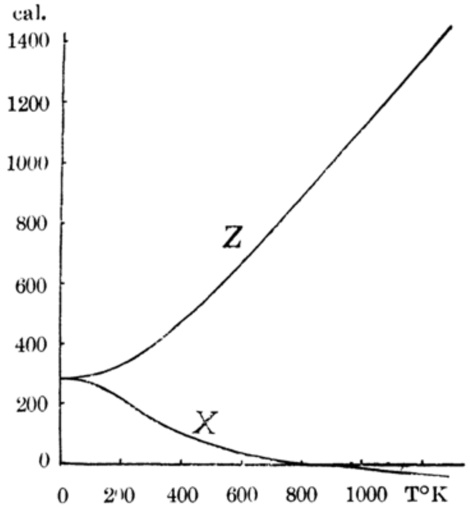
(6) W. A. Roth and H. Wallasch, *Z. Elektrochem.*, **21** (1915), 1.

(7) W. Nernst, *Ann. Physik*, **36** (1911), 396.

(8) A. Magnus and A. Hodler, ibid., **80** (1926), 808; A. Magnus, ibid., **70** (1923), 303.

calculation of the specific heats at the lowest temperatures, and the method of graphical integration has been used for the higher temperature. The results obtained are shown in the following table and in Fig. 1. In which $X\quad \chi_{\text{diamond}}-\chi_{\text{graphite}}$ and $Z=\zeta_{\text{diamond}}-\zeta_{\text{graphite}}$. Therefore Z may be understood as the affinity of transition and X the heat of transition from diamond to graphite.

T°K.	X cal./gr. atom.	Z cal./gr. atom.
0	277	277
100	264	283
200	212	318
300	150	386
400	100	471
500	62	568
600	35	672
700	15	780
800	2	890
900	− 4	1007
1000	−16	1116
1100	−24	1230



Diamond and Graphite.

Fig. 1

These values will also be reproduced within the limits of a few percent if we apply the Debye's functions for the specific heats,

$$c_{p\ \text{diamond}}=D\left(\frac{1900}{T}\right)+1.9\times10^{-6}\,T^{\frac{3}{2}}\ ;$$

$$c_{p\ \text{graphite}}=\frac{1}{3}\left[2D\left(\frac{2280}{T}\right)+D\left(\frac{760}{T}\right)\right]+4.0\times10^{-6}\,T^{\frac{3}{2}}$$

where

$$D\left(\frac{\theta}{T}\right)=3Nk\left[\frac{12}{x^3}\int_0^{\infty}\frac{\xi d\xi}{e^{\xi}-1}-\frac{3x}{e^{x}-1}\right],$$

$$x=\frac{\theta}{T}=\frac{h\nu_{\text{max.}}}{kT}\quad\text{and}\quad\xi=\frac{h\nu}{kT}.$$

The nature of the Z-curve in Fig. 1 shows that graphite is more stable than diamond in the range from 0°K. to 1100°K. And it is a well known fact that diamond is unstable at the higher temperatures above it. Out of these considerations, we are able to confirm that the dimorphism of diamond and graphite is truly monotropic, instead of being pseudomonotropic.

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(1) P. Debye, *Ann. Physik*, 39 (1912), 789.

(2) Strictly speaking, it is necessary to add the condition, " under the atmospheric pressure," however, it will be omitted when clear.

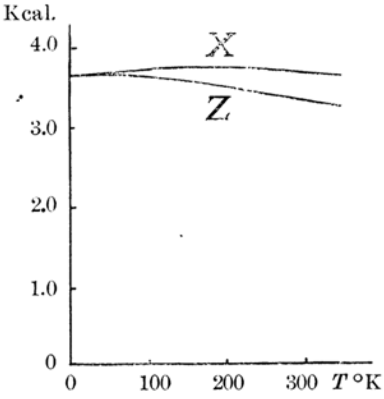
Furthermore, the *X*-curve in Fig. 1 shows that the heat of transition changes its sign at ca. 850°K. Above this temperature diamond seems to transform into graphite with the absorption of heat. It had been considered by some authors as one of the characteristic properties of monotropy that the unstable modification changes into the stable with the evolution of heat.(1) However, it may be mentioned here that even if there exist always stable and unstable modifications, the transition will not always occur with the evolution of heat, as is clear by the behaviours of *Z*- and *X*-curves in Fig. 1.

An analogical case will be found in the dimorphism of white and red phosphorus. As red phosphorus is nonvolatile and practically insoluble in many solvents below the ordinary temperature, it is also difficult to estimate the affinity of transition between them directly. Similar estimation on the basis of the Nernst's theorem have been carried out. As for the heat of transition, the Giran's(2) data have been taken,

Red phosphorus = White phosphorus + 3.70 Kcal./gr. atom (290°K.)

With regard to the specific heats, the data of Wigand(3) and Ewald(4) have been taken. The data of the specific heats are not very accurate in this case. However, the heat of transition is so large that the accuracy of the specific heats has no much influence upon the evaluation of the affinity of transition and the heat of transition. The results are shown in the following table and in Fig. 2, in which *Z* and *X* are the affinity and the heat of transition from white to red phosphorus respectively.(5)

T °K.	*X* Kcal./gr. atom	*Z* Kcal./gr.atom.
0	3.67	3.67
50	3.69	3.66
100	3.75	3 61
150	3.77	3.54
200	3.76	3.47
250	3.73	3.39
300	3.69	3.33



White and Red Phosphorus.
Fig. 2.

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(1) H. W. B. Roozeboom, loc. cit.; cf. the quotation of O. Lehmann in the preceeding paper.

(2) Giran, *Ann. chim. phys.*, 30 (1903), 203.

(3) A. Wigand, *Ann. Physik*, 22 (1907), 64.

(4) R. Ewald, ibid., 44 (1914), 1213.

(5) As white phosphorus has a transition point at ca.–78°C., the white phosphorus above given is the form with the melting point at 44°C. cf. Bridgman, *J. Am. Chem. Soc.*, 36 (1914), 1244.

The affinity curve in Fig. 2 shows that red phosphorus is more stable than white phosphorus from absolute zero to the melting point of the white phosphorus. It is, therefore, truly monotropic, although it was supposed to be pseudomonotropic by Findlay.(1)

In certain cases of dimorphism, however, one modification exists in a very narrow range of temperature. So that the above given method to determine the relation ef mutual stability on the rigorous bases of the second law and the Nernst's theorem will fail, for the specific heats will not completely be measured. If the melting points and the latent heats of fusion of the both forms are known, however, we are able to derive an approximation formula for the estimation of the affinity of transition. After Nernst we may put, for the first approximation, that

$$X = X_0 + \beta T^2 \quad \text{and} \quad Z = X_0 - \beta T^2.$$

If we apply these formulae to the relations between the liquid phase and the modification A, we have

$$X_A = \chi_l - \chi_A = X_{A0} + \beta_A T^2\,, \qquad \text{.................}(5)$$

and

$$Z_A = \zeta_l - \zeta_A = X_{A0} - \beta_A T^2\,, \qquad \text{.................}(6)$$

where χ_l and ζ_l are the specific values of χ- and ζ-functions of Gibbs concerning the liquid phase respectively.

At the melting point T_A, we have $Z_A = 0$. Therefore, from (6), we have

$$\beta_A = \frac{X_{A0}}{T_A^2}\;.$$

Putting it in (5), we have

$$X_{A0} = \frac{1}{2}\lambda_A \quad \text{and} \quad \beta_A = \frac{1}{2}\frac{\lambda_A}{T_A^2}\;,$$

where λ_A is the heat of fusion at the melting point T_A: Accordingly we have

$$Z_A = \frac{1}{2}\lambda_A - \frac{1}{2}\frac{\lambda_A}{T_A^2}T^2\;.$$

Similarly

$$Z_B = \frac{1}{2}\lambda_B - \frac{1}{2}\frac{\lambda_B}{T_B^2}T^2.$$

where $Z_B = \zeta_l - \zeta_B$, λ_B being the latent heat of fusion at the melting point T_b of the modification B.

Henceforth we have,

$$\begin{aligned} Z = \zeta_B - \zeta_A &= Z_A - Z_B = X_0 - \beta T^2 \\ &= \frac{1}{2}(\lambda_A - \lambda_B) - \frac{1}{2}\left(\frac{\lambda_A}{T_A^2} - \frac{\lambda_B}{T_B^2}\right)T^2 \qquad \text{.................}(7) \end{aligned}$$

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(1) A. Findlay, "The Phase Rule" (1920); p. 48.

or

$$X_0 = \frac{1}{2}(\lambda_A - \lambda_B) \quad \text{and} \quad \beta = \frac{1}{2}\left(\frac{\lambda_A}{T_A^2} - \frac{\lambda_B}{T_B^2}\right).$$

Putting $Z=0$, we have the transition temperature T_0 between the two modifications A and B,

$$T_0 = \left(\frac{\lambda_A - \lambda_A}{\dfrac{\lambda_A}{T_A^2} - \dfrac{\lambda_B}{T_B^2}}\right)^{\frac{1}{2}} \qquad \text{.............(8)}$$

With regard to the dimorphism of sulphur,(1)

$T_A = 388^\circ$K., $\lambda_A = 15.7$ cal./gr. (rhombic sulphur)
and $T_B\ 392^\circ$K., $\lambda_B = 12.5$ cal./gr. (monoclinic sulphur)

Putting these values in the formulae (7) and (8), we have

$Z = 1.60 - 1.16 \times 10^{-5} T^2$ cal./gr.,
and $T_0 = 372^\circ$K. (obs. 368°K.)(2)

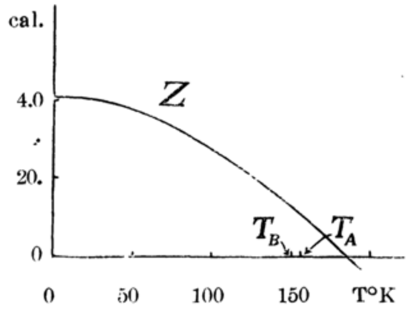
As for ethyl ether, we have following data,

$T_A = 157^\circ$K., $\lambda_A = 27.0$ cal./gr.,(3)
and $T_B = 150^\circ$K., $\lambda_B = 18.9$ cal./gr.(4)

Accordingly we have,

$Z = 4.05 - 2.53 \times 10^{-4} T^2$ cal./gr.
and $T_0 = 177^\circ$K. (above the melting points of the two modifications).

The values obtained by the above formula are shown in Fig. 3, which shows that the modification with the melting point at 150°K. is more stable than the modification with the melting point at 150°K., in the range from 0°K. to 177°K. We may therefore consider that this dimorphism of ethyl ether is monotropic.



Dimorphism of Ethyl Ether

Fig. 3

Although it is difficult to expect much accuracy from it, we are able to find that similar monotropic relations also hold for the dimorphisms in iodine monochloride,(5) benzophenone, bromonitrobenzene, phthalide, acetamide, monochloracetic acid, nitro-*p*-toluide and erythrite.(6) The values of X_0 and β are shown in the following table together with the data necessary for their evaluations.

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(1) G. Tammann, "Kristallisieren und Schmelzen" (1903), p. 273.

(2) The results are in good coincidence with the estimation of Nernst, who obtained β by the data of specific heats.

(3) Beckmann and Waentig, *Z. anorg. allgem. Chem.*, **67** (1910), 17.

(4) S. Mitsukuri, this journal, **1** (1926), 30.

(5) Stortenbeker, *Z. physik. Chem.*, **10** (1892), 187.

(6) A. H. R. Müller, ibid., **86** (1913), 237.

Substance	T_A °K	λ_A cal./gr.	T_B K°	λ_B cal./gr.	X_0 cal./gr.	$\beta\times 10^5$
Iodine monochloride	300	16.4	287	14.0	1.20	0.60
Benzophenone	321	23.4	298	17.9	2.75	1.25
Bromonitrobenzene	332	29.3	308	21.0	4.15	2.75
Phthalide	346	39.4	333	20.0	9.70	7.40
Acetamide	355	66.1	344	57.0	4.55	2.05
Monochloracetic acid	334	40.7	329	35.2	2.75	1.85
Nitro-p-toluide	366	30.0	365	26.7	1.65	1.15
Erythrite	390	43.7	377	38.0	2.85	1.00

In short, if the two modifications have a sharp transition point, it may be easy to ascribe it to enantiotropy. However, even if we observe the transition only in one direction within a limited range of temperature, it is rather difficult to ascribe it to monotropy. For the phase changes between the two modifications are often disturbed by the effects of retardation, and in certain occasions, the enantiotropic dimorphism may manifest itself like monotropic. It may form one of the cases of pseudomonotropy. Accordingly, if we would to ascribe any dimorphism to monotropy, the affinity of transition should be estimated over a wide range of temperature. Although we know of many cases supposed to be monotropic, the affinities of transition connected to them have not fully been testified so far. In the above discussions, it has been tried to estimate the affinity of transition for such cases.

Effects of Pressure on the Affinity of Transition. In the preceeding paragraphs, the effects of pressure on the mutual stability of dimorphism have not been estimated. The affinity of transition under high pressure will be estimated by the formula (4), by which it is meant that we are able to estimate the affinity of transition at any pressure p if we know the affinity of transition at certain pressure p_1 and the specific volumes of the two modifications between p_1 and p. Therefore, it may be able to determine whether or not it is enantiotropic under high pressure, if we know the affinity of transition at one atmospheric pressure and the necessary data of the specific volumes. As for the case of diamond and graphite, we have

$$\begin{aligned} V &= v_{\text{diamond}} - v_{\text{graphite}} \\ &= 12(1/3.5 - 1/2.3) = -1.79 \text{ cm.}^3/\text{gr. atom. (1 atm.)} \end{aligned}$$

For the first approximation, we may put

$$\begin{aligned} \int_1^p V dp &= p V \\ &= -1.79\, p \text{ atm. cm.}^3/\text{gr. atom.} = -0.0433\, p \text{ cal./gr. atom.} \end{aligned}$$

As we have gained (page 212) that $Z_{300°\text{K.}} = 386$ cal./gr. atom., and $\int_1^{10000} V dp$

$= -433$ cal./gr. atom., we may consider that there will be a transition point at 300°K, under the pressure of ca. 10^4 atms. and that the case of diamond and graphite is probably enantiotropic under the pressure of ca. 10^4 atms. Whereas in the case of white and red phosphorus, the affinity of transition is enormous and $V = +3.17$ cm^3/gr. atom (1 atm.). Therefore it will remain monotropic even under the farly high pressure.

In conclusion, the author wishes to express his hearty thanks to Prof. J. Sameshima whose counsels have been constantly at his disposal.

Summary

1. The affinity of transition and the heat of transition from diamond to graphite and from white phosphorus to red phosphorus have been evaluated on the basis of the Nernst's theorem and it has been made clear that they are monotropic under the atmospheric pressure. The former case will probably be enatiotropic under high pressure, whereas the latter case will remain monotropic even under high pressure.

2. An approximation formula for the estimation of the affinity of transition has been derived and by means of which the dimorphisms in ethyl ether, iodine monochloride, benzophenone, phthalide, bromonitrobenzene, acetamide, monochloracetic acid, nitro-*p*-toluide and erythrite have been estimated to be monotropic.

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