

Chemistry. — *The Exact Measurement of the Specific Heats of Solid Substances at Higher Temperatures. XIV. The Specific Heats and Thermal Retardation-Phenomena of Beryllium.* By F. M. JAEGER and E. ROSENBOHM.

(Communicated at the meeting of January 27, 1934.)

§ 1. In two successive papers from this laboratory¹⁾, we have drawn attention to the remarkable retardation-phenomena, which occur if compact, crystalline *beryllium* is heated at temperatures of 500° or 600° C. and then is dropped into the calorimeter; and to the occurrence of new diffraction-lines in the *X*-rayspectrum of the metal, if this be heated for a long time at 630° C., — these new lines apparently corresponding to another hexagonal structure of the metal, which was called by us the β -modification, in contrast to the ordinary α -form.

In the first place, we now have studied the said retardation-phenomena more in detail, especially since we observed apparently analogous phenomena in the case of *zirconium* and *thorium*. Lumps of beautifully crystallized, macrocrystalline *beryllium* were enclosed in an evacuated platinum crucible and very carefull measurements of its specific heats were made in the vicinity of 300°, 350° and 400° C. Soon it became clear that a distinct influence of the duration of the heating and subsequent cooling on the numerical valeus of \bar{c}_p can be stated. In Fig. 1 the values of \bar{c}_p observed in a series of such experiments are graphically represented. They clearly show, that a sample of the metal, which was not yet subjected to preliminary heatings, manifests a rapid increase of \bar{c}_p at about 388° C., while between 399° and 410° C. \bar{c}_p remained practically constant (curve I); the sudden break in the curve, however, proves in subsequent heatings, gradually to be smoothed-out, as is seen from the curves II—IV. The values of \bar{c}_p , moreover, prove to be strongly variable at the same temperature. This fact doubtlessly demonstrates, that a change in the metal occurs, which during the interval of time elapsed after its heating and cooling, does not completely go back: the metal does *not* return to its original condition²⁾.

¹⁾ F. M. JAEGER and E. ROSENBOHM, *Proceed. R. Acad. Sciences Amsterdam*, **35**, (1932), 1055; F. M. JAEGER and J. E. ZANSTRA, *ibidem*, **36**, (1933), 636.

²⁾ The numbers between () indicate the series-numbers of the subsequent heatings; each experiment took about one day.

A great number of successive experiments was made, — care being taken not to heat the metal above 410° C. The results obtained are collected

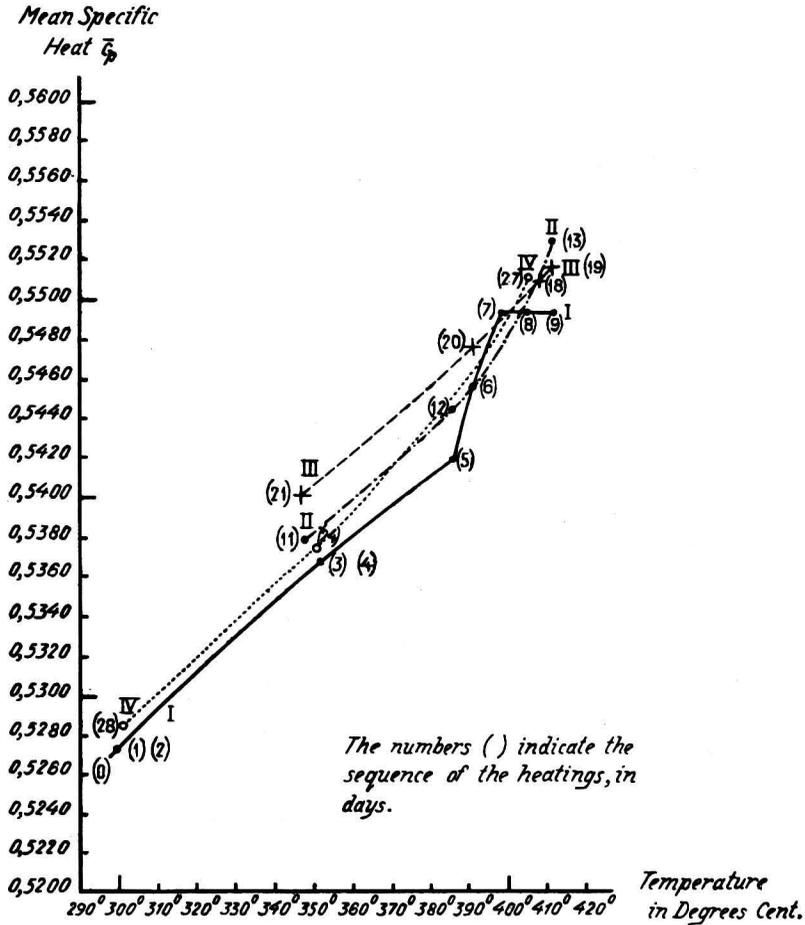


Fig. 1. Variability of \bar{c}_p of Beryllium on repeatedly Heating.

in Table I and graphically represented in Fig. 2, in which the values of \bar{c}_p

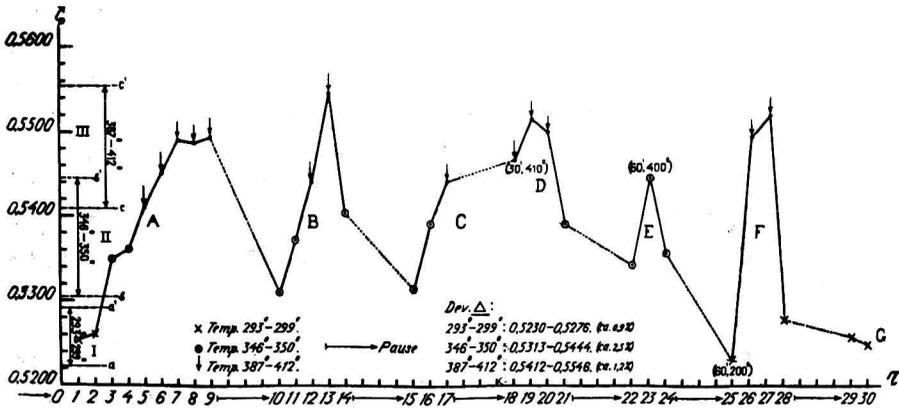


Fig. 2. Variability of \bar{c}_p of Beryllium with the time τ of Heating and cooling

TABLE I.
Variations of \bar{c}_p of Beryllium with Time of Heating and Cooling.

Sequence of Heatings and Time τ elapsed in Days:	Temperature t °C. of Measurement:	Value of the Mean specific Heat \bar{c}_p observed:
1	297°.79	0.5258
2	293.71	0.5262
3	347.52	0.5350
4	348.00	0.5362
5 } Series A	387.25	0.5413
6	391.71	0.5451
7	393.67	0.5487
8	399.79	0.5488
9	409.32	0.5487
Pause of 3 days		
10	346.41	0.5313
11	349.43	0.5376
12 } Series B	386.92	0.5441
13	412.55	0.5545
14	350.64	0.5407
Pause of 3 days		
15	346.30	0.5313
16 } Series C	347.53	0.5391
17	391.73	0.5440
Pause of 3 days, (first heated 30 Min. at 410° and then 3 hours at 392°.32)		
18	392.32	0.5468
19 } Series D	410.52	0.5516
20	408.26	0.5502
21	347.65	0.5393
Pause of 3 days		
22	347.60	0.5337
(first heated 60 Min. at 400° and then 3 hours at 348°.7 C., etc.)		
23	348.73	0.5444
24 } Series E	347.45	0.5360
Pause of 3 days, (first heated 60 Min. at 200° and then 3 hours at 296°.84 C., etc.)		
25	296.84	0.5229
26 } Series F	408.09	0.5495
27	406.07	0.5518
28	299.25	0.5275
Pause of 3 days		
29	298.14	0.5257
30 } Series G	298.38	0.5250

observed are plotted against the time τ elapsed between the subsequent heatings. The seven series (A—G) of experiments cover an interval of about 48 days. Within the field aa' all values of \bar{c}_p between 293° and 299° C. are represented; within bb' all those between 346° and 350° C.; within cc' those between 387° and 412° C. At once it becomes clear, that a heating at a constant higher temperature t' causes the value of \bar{c}_p at a given lower temperature t to *increase* with respect to the value formerly observed at that temperature t ; on the other hand, that the value of \bar{c}_p previously found at t° , always appears noticeably to be *diminished*, if the sample be kept at room-temperature for three days and only increases again, if the metal be heated a second time.

The deviations of \bar{c}_p at temperatures between 293° and 299° C. amount to 1 %, those between 346° and 350° C. to about 2.5 %, those between 387° and 412° C. to about 1.2 % of the absolute values and are, therefore, 10—20 times greater than the mean experimental error of the method used. Within certain limits, at each temperature one can find all arbitrary values of \bar{c}_p at any temperature t , — these being wholly dependent on the preliminary thermal treatment of the metal and the time τ since elapsed. In these experiments the time-interval between the moment of dropping the sample into the calorimeter and that at which the maximum temperature t'' of the calorimeter was reached, originally was 16 minutes; but as soon as the metal is heated above 500°—600° C. this interval increases enormously: at 500° C. to 25, at 630° to 45, at 800° C. to 53 minutes, and it still remains 53 minutes, even after returning to 370° C. The complete recurrence of the metal into its original condition takes longer than 9 or 10 months; but it is highly remarkable, that even after so short a time as 3 days, a distinct recurrence towards this "normal" state already proves to be observable.

§ 2. A bar of *beryllium* of American origin manifested these phenomena to a still higher degree than the German preparation, — the interval mentioned here being more than 1½ hours. Suspicion arose, that the dimensions of the lumps used might perhaps prove also to play a role in the behaviour of the metal, — the more as the experience gathered in the case of *zirconium* and *thorium* pointed into the same direction. Therefore, the sample used in the foregoing experiments was preliminarily divided into two portions and one half very finely ground and the powder thus obtained enclosed within an evacuated platinum crucible. This time, the heat-development proved to be quite "normal" indeed: between 100° and 1065° C. no retardation-effect now was any more stated, so that the values of Q_0 could be determined with a fair degree of accuracy. The results of these measurements are represented in Table II. The mean specific heats \bar{c}_p can be expressed by:

$$\bar{c}_p = 0,414032 + 0,359947 \cdot 10^{-3} \cdot t - 0,740474 \cdot 10^{-7} \cdot t^2 - \\ - 0,359176 \cdot 10^{-9} \cdot t^3 + 0,313094 \cdot 10^{-12} \cdot t^4.$$

TABLE II.
The Mean Specific Heats of "normal" Beryllium.

Temperature t of Observation:	Final temperature t' of the Calorimeter:	Quantity of Heat Q developed between t and t' by 1 Gr. of the metal:	Quantity of Heat Q_0 developed by 1 Gr. of the metal between t and 0 °C.:	Mean Specific Heat \bar{c}_p	
				(observed):	(calculated from the formula):
99.80	20.375	36.100	44.800	0.4489	—
99.84	20.377	36.118	44.818	0.4489	—
197.73	20.89	85.454	94.374	0.4773	0.4800
296.93	21.09	141.77	150.78	0.5078	0.5079
298.72	21.17	142.67	151.71	0.5079	—
392.53	21.27	199.01	208.09	0.5301	0.5297
392.90	21.37	199.30	208.42	0.5305	0.5300
417.31	20.97	214.21	223.16	0.5347	0.5347
439.57	21.50	227.59	236.77	0.5386	0.5391
450.79	21.69	234.74	244.00	0.5413	—
499.56	21.06	266.09	275.08	0.5506	0.5501
549.58	21.73	297.69	306.98	0.5586	0.5584
631.35	21.57	351.36	360.58	0.5711	—
801.69	22.66	470.75	480.43	0.5993	—
1064.97*	23.02	(650.80)	(669.63)	(0.6288)	(0.6823)

* At this temperature the platinum crucible proved to be somewhat attacked by the metal. Weight of the platinum crucible = 27.2994 Gr.; weight of the beryllium: 4.1682 Gr.

Therefore, the true specific heats c_p by:

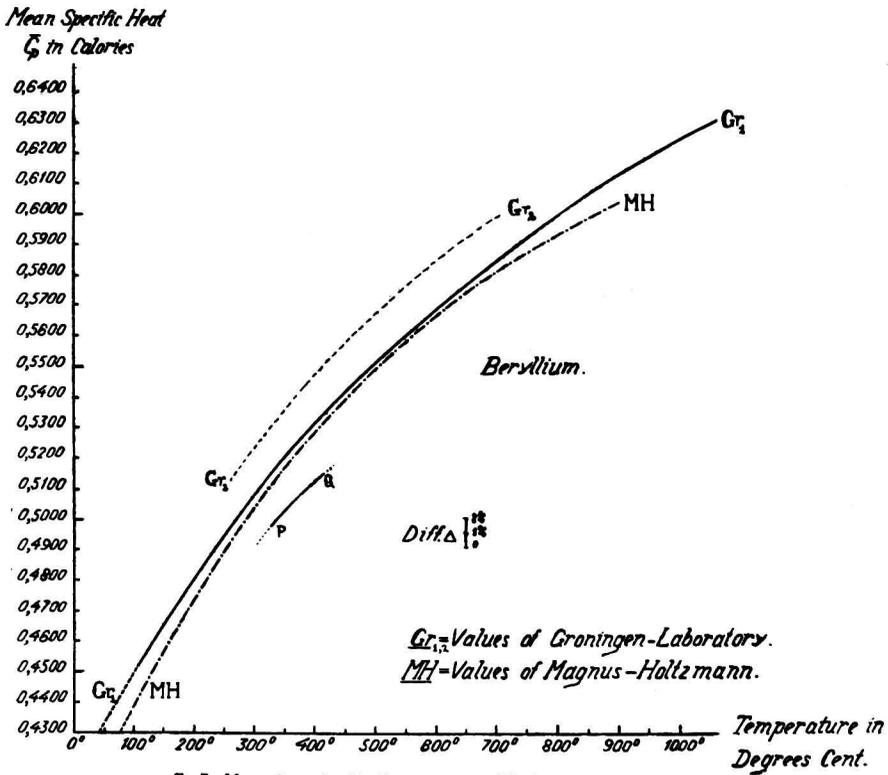
$$c_p = 0,414032 + 0,719894 \cdot 10^{-3} \cdot t - 0,2221422 \cdot 10^{-6} \cdot t^2 - \\ - 0,1436704 \cdot 10^{-8} \cdot t^3 + 0,156547 \cdot 10^{-11} \cdot t^4.$$

and the atomic heats C_p by:

$$C_p = 3,73457 + 0,64935 \cdot 10^{-2} \cdot t - 0,20037 \cdot 10^{-5} \cdot t^2 - \\ - 0,12959 \cdot 10^{-7} \cdot t^3 + 0,14122 \cdot 10^{-10} \cdot t^4.$$

Some of the values of c_p and C_p thus calculated are collected in Table III and graphically represented in Fig. 4.

In the first place it can be remarked that the only difference between this "normal" and the formerly used "abnormal" *beryllium* is the *degree of division* of the metal and a slight superficial oxydation. On pulverisation of the metal, the finely divided particles of this very easily oxydizable metal become surrounded by an extremely thin layer of berylliumoxide and this, evidently, prohibits the change, locally started on heating, to



spread through the whole mass. In this way no additional heat-development is any longer observed and the sample apparently behaves in a "normal" way. But this "normal" state is, properly speaking, an "abnormal" condition of the metal, as it corresponds to an innerly-paralysed condition. The values of \bar{c}_p measured with this powder, are in Fig. 3 represented by the curve Gr_2 , which lies somewhat higher than the more probable curve Gr_1 , (see Table II), determined with a sample of the same origin as that used by MAGNUS and HOLZMANN¹⁾, who did not observe any retardation-phenomena. Their values of \bar{c}_p (curve MH in Fig. 3) are in fairly good agreement with ours; but all these values, corresponding to samples containing more or less *berylliumoxide*, probably are *somewhat too high* (3 or 3.5 %). The points P and Q in Fig. 3 correspond to the

¹⁾ A. MAGNUS and H. HOLZMANN, Ann. d. Phys. 3, (1929), 585.

TABLE III. True specific and atomic Heats c_p and C_p of "normal" Beryllium.		
Temp. t° :	True specific Heat c_p :	Atomic Heat C_p :
0°	0.4140	3.734
100	0.4825	4.352
200	0.5402	4.872
300	0.5839	5.267
400	0.6149	5.546
500	0.6364	5.740
600	0.6585	5.940
700	0.6924	6.246
800	0.7536	6.797
900	(0.8617)	(7.772)

values: $\bar{c}_p = 0,4978$ at $327^\circ,5$ C. and $\bar{c}_p = 0,5145$ at $419^\circ,4$ C., determined with a lump of *beryllium* not yet previously heated; the curve for this non-heated, compact material presumably seems to be about parallel to the curves Gr_1 and Gr_2 .

In the second place Fig. 4 teaches us that the curve for the true specific and atomic heats has an *inflection-point* S : the existence of this inflection-point also may be deduced from the formula of MAGNUS and HOLZMANN for c_p . It is situated between 506° and 638° C., — the latter value being calculated from the measurements of the German authors, and its place seems to correspond fairly well to values of the atomic heat in the neighbourhood of $3R$ calories, — C_p subsequently increasing at higher temperatures in an appreciably steeper way than before.

§ 3. The phenomena observed doubtlessly prove, that in the case of *beryllium* we have to deal with an *inner dynamical or mobile equilibrium of two different constituents of the metal*. The change certainly is of a *reversible* nature; but evidently strong passive resistances and retarding influences prohibit the complete establishment of the equilibrium at each temperature. Moreover, the recurrence of the high-temperature condition of the metal into that characteristic for lower temperatures, must be *exothermic*, i.e. must be accompanied by a development of heat.

If the α - and β -modifications of *beryllium* previously observed¹⁾ are

¹⁾ F. M. JAEGER and J. E. ZANSTRA, loco cit. Evidently the supposition of a monotropic relation between the two forms of the metal, must be rejected, after the true reversibility of the phenomena now has been established.

these components in the mobile equilibrium mentioned, then these equilibria at a whole series of temperatures only could occur *within a single*

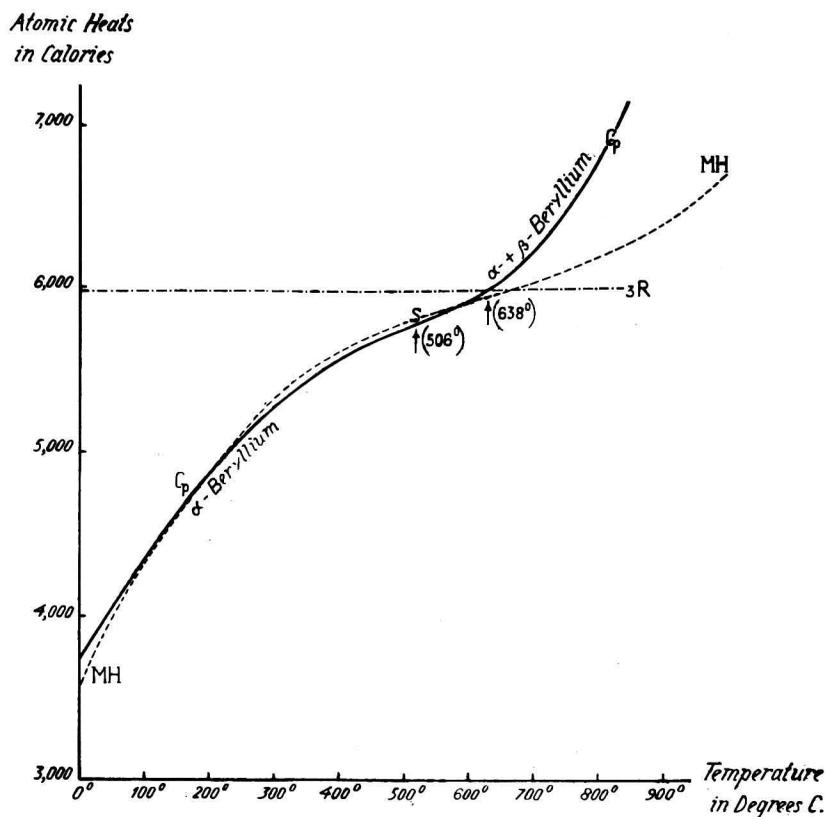


Fig. 4. Atomic Heats of „normal” Beryllium.

homogeneous phase of varying composition, i.e. within a mixed crystal or solid solution of α - and β -beryllium. But the difficulty here arising is, that the X-ray-analysis does not give any indication of the presence of such a solid solution: on the contrary, the spectra of the α - and the β -forms always do appear *besides* each other and they thus rather correspond to a mere *juxtaposition* of both lattices involved.

Prof. SMITS, to whom we are obliged to a number of valuable remarks in this respect, suggested to us, that the present case of metallic *beryllium* might perhaps better be understood as an example of a mobile, internal equilibrium of two “pseudo-components” δ and ε , which is shifted in the one or in the inverse direction by a change of the temperature. In this respect, he finally drew our attention to the possibility, that these two pseudocomponents might form a dimorphous series of mixed crystals in the solid phase showing a hiatus; so that *two* limiting, saturated mixed crystals of different compositions and both corresponding to the α -, respectively β -spectra observed, are at each temperature co-existent, —

the one kind (α -form) containing a large excess of the δ -component, the other kind (β -form) a large excess of the other component.

Below about 630°C , δ - and ε -beryllium then should behave as *real* components, not transformable into each other, while at much higher temperatures most probably an internal homogeneous equilibrium between them, as in a true pseudo-binary system would prove to exist. On cooling, the composition of each saturated mixed crystal then normally should be shifted along the two boundary-lines of the diagram; but the complete establishment of these successive heterogeneous equilibria evidently goes on in so extremely slow a way, that a very long interval of time is necessary for its total accomplishment. For this reason the retardation-phenomena described then are observed in the way mentioned above. The momentaneous state of the metal, — as composed of these two kinds of saturated mixed crystals, — cannot be indicated with any degree of certainty, as i.a. it depends on the more or less accidental content of δ - and ε -beryllium, acquired in the original process of preparation of the metal. The α - and β -spectra observed besides each other, thus must correspond to the two different types of saturated mixed crystals, co-existing at each temperature.

Even if this interpretation of the facts be true, the difficulty remains, that it is hardly possible to imagine *what* the two supposed constituents of the metallic phase possibly could be? SMITS in this respect suggests two possibilities: either there are two kinds of special arrangements of beryllium-atoms, which perhaps, in some way or other are connected with a formation of molecular aggregations ¹⁾; or there are two kinds of beryllium-atoms present, due to the internal fields of force resulting from the mutual interaction of the atoms in the crystalline state ²⁾. But in the latter case, the rather unusual assumption then must be made, that the atoms in these different states cannot be transformed into each other.

In our opinion, both suppositions seem to be rather hazardous ones in the case of so simply built and stable atoms as those of beryllium, which only possess 4 electrons of a low energy-level in two successive orbits.

Finally it can be remarked, that it were equally well possible that the occurrence of the β -spectrum is a phenomenon quite apart from the manifestation of the retardation-phenomena described. Considering all

¹⁾ In this respect attention may be drawn to the interesting case of the complex compounds: Cu_2HgI_4 and Ag_2HgI_4 studied by KETELAAR (*Thesis*, Amsterdam, (1933), 43), where the pseudo-components were identified by this author with two different structure-types and the two occurring modifications were considered as mixed crystals containing the two types in different proportions.

²⁾ A greater number of different states of the atoms in the solid phase can be expected for this reason, than in the gaseous state. According to these view, energy-differences between these states occasionally may appear, according to SMITS, varying from as little as 1 calorie or less, — as in the case of the rare earth-metals, — up to several thousands of calories.

facts, we can say that, although the hypothesis of an internal equilibrium between two constituents appears an alluring one, the true nature of these still remains unknown.

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Physics. — *On anomalies of terrestrial magnetism.* By S. W. VISSER.

(Communicated at the meeting of December 16, 1933.)

1. BAUER (1), NIPPOLDT (2), BARTELS (3), ANGENHEISTER (4) have expressed objections to GAUSS's method of spherical harmonics of the field of terrestrial magnetism.

Therefore a new research into the normal field appears to be justified. We have based our investigation wholly upon the isomagnetic maps of the Hydrographic Office, Navy Department U.S.A., Washington 1930. As to the north-polar cap we have also consulted FISK's maps (5). This suffices for our purpose being a first orientation.

We shall derive in the first place some properties of a "normal field" based upon two adiametrical poles, presuming them to have equal strength.

2. We call the straight line between the poles the "magnetic axis". The great circle perpendicular to this axis will be called "magnetic equator". Furthermore we call the small circles through the magnetic poles "magnetic meridians". The great circle through the poles will be the zero-meridian of our system.

The magnetic equator and the zero-meridian have been taken as axes of coordinates. The origin is one of the two points where these great circles intersect. It is situated in the centre of the Pacific Ocean at 146.6° W.L. in the immediate neighbourhood of the geographic equator. The angle between the magnetic and geographical equatorial planes amounts to 15 degrees.

The distance of the poles to the origin is 78.0° . Each magnetic meridian has been divided between the equator and the poles into 78 equal parts and curves have been drawn through corresponding points. These curves may be suitably called "parallels" and the 78 equal parts "degrees". Points on the sphere will be located by means of the meridians and parallels of this system.

3. We may presume now the following properties of our "normal field".

1. The inclination is zero along the magnetic equator and reaches a maximum value at the poles.