Liest man diese Gleichung in umgekehrter Richtung, so sieht man, dasz (Hx, y') ein für $x \in \mathfrak{D}$ beschränktes Funktional (im Sinne von $\mathfrak{R}$) ist. Also ist y' in $\mathfrak{D}^*$, also auch im Durchschnitt von $\mathfrak{R}'$ und $\mathfrak{D}^*$, also $y' \in \widetilde{\mathfrak{D}}$ und $\tilde{H} y' = y$. Da y willkürlich in $\mathfrak{R}$ war, bedeutet das $H \widetilde{\mathfrak{D}} = \mathfrak{R}$. Nach J. v. NEUMANN [2]) ist also $\tilde{H}$ selbstadjungiert.

2. $\tilde{H}$ hat dieselbe untere Grenze wie H. K. FRIEDRICHS [3]) hat gefragt, ob $\tilde{H}$ als selbstadjungierte Fortsetzung von H durch diese Eigenschaft charakterisiert sei. Wir verneinen die Frage:

$\mathfrak{R}$ sei direkte Summe der Hilbertschen Räume $\mathfrak{R}_1$ und $\mathfrak{R}_2$; H_1 sei in $\mathfrak{R}_1$ definiert als der identische Operator, H_2 in $\mathfrak{D}_2 \subset \mathfrak{R}_2$ als halbbeschränkter Hermitescher Operator mit der unteren Schranke $\gamma > 1$; H sei die direkte Summe von H_1 und H_2. H'_2 sei irgendeine selbstadjungierte Fortsetzung von H_2 in R_2 mit einer zwischen 1 und γ liegenden unteren Schranke. H'_2 wird im allgemeinen von $\tilde{H}_2$ verschieden sein (z. B. wenn $\mathfrak{R}_2$ der Raum der im Einheitsintervall zweimal stetig differenzierbaren Funktionen ist, die in den Endpunkten mit samt ihren ersten Ableitungen verschwinden, und H_2 die Bildung der negativen zweiten Ableitung). H', die direkte Summe von H_1 und H'_2, wird dann auch von $\tilde{H}$ verschieden sein, aber doch dieselbe Schranke wie H (nämlich 1) besitzen und selbstadjungiert sein.

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[2]) Math. Ann. **102**, 49—131 (1929). Insbesondere Satz 41.

[3]) a a. O., Fusznote 14.

Chemistry. — *The Exact Measurement of the Specific Heats of Metals at High Temperatures:* **XXV.** *The Specific Heats and the Allotropism of Nickel between 0° and 1000° C.* By M. EWERT. (Communicated by Prof. F. M. JAEGER.)

(Communicated at the meeting of June 27, 1936).

§ 1. The data about the allotropism of *nickel*, as given in the literature [1]), are still rather confusing. Certainly there is a cubic, face-centred α-form with $a_0 = 3.518$ A.U. and a density of 8.86 stable at ordinary temperatures to about 350° C. Exactly as in the case of cubic, body-centred α-iron at 768° C. and in that of hexagonal α-*cobaltum* at 1105°—1130° C., the change of α-*nickel* at 350°—353° C. from the

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[1]) For the literature cf.: F. M. JAEGER and E. ROSENBOHM, Proc. Royal Acad. Amsterdam, **34**, 818 (1931); Rec. d. Trav. d. Chim. Pays-Bas, **51**, 41 (1932).

ferromagnetic into the feebly paramagnetic β-state *is not accompanied by a change in the crystalline structure*. In how far the said transformation which, from the calorimetrical point of view, has the complete character of an allotropic change, really has to be considered as a case of true "allotropism", depends on the definition adopted for the latter phenomenon: here the indication of α- and β-states is given conform to the indication of α- and β-*iron*. Moreover, BREDIG and ALLOLIO [1]) proved that another, closest-packed hexagonal form of *nickel* exists, which already at about 300° C. would be transformed into the ordinary cubic form; this hexagonal α'-*nickel* would have the parameters: $a_0 = 2.684$ A.U. and $c_0 = 4.382$ A.U. and a density of 7.04.

The low density gave rise to the supposition, that these authors really studied a *hydride* of hexagonal *nickel*: indeed, THOMPSON, by means of electron-diffraction experiments, afterwards confirmed the existence of the hexagonal modification, but found: $a_0 = 2.474$ A.U.; $c_0 = 4.06$ A.U. and $d = 8.86$, — which agrees much better with the density of the ordinary cubic form.

Hitherto it was unknown in what relation this hexagonal modification stood with respect to the cubic form. From measurements of the heat-capacity according to SALADIN-LE CHATELIER's twin-galvanometer method [2]) and from analogous determinations of the electrical resistance [3]) and of the thermo-electrical behaviour towards *copper* [4]) as a function of the temperature, JAEGER and ROSEMBOHM drew the conclusion that most probably the hexagonal α'-form of the metal equally is an enantiotropic form, its province of stability being situated between those of the α- and β-states. By this supposition the characteristic peculiarities of the transformation α-$\rightleftarrows$ β-*nickel*, as observed by them and other investigators with respect to the ever more or less "gradual" changes of the physical properties of the metal, would simultaneously find a ready explanation.

The results of the calorimetrical experiments communicated in the present paper now most probably can be considered to prove the exactness of the supposition mentioned: the shape of the Q_0-t-curve clearly

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[1]) G. BREDIG and R. ALLOLIO, Zeits. phys. Chem., **126**, 41 (1917); G. BREDIG und E. SCHWARZ VON BERGKAMPF, ibidem, BODENSTEIN-Bnd, 172 (1931); W. BÜSSEM und F. GROSS, Zeits. f. Phys., **87**, 778 (1934); E. R. JETTE, V. H. NORDSTROM, B. QUENAU und F. FOOTE, Amer. Inst. Min. Met. Engin. Publ. N⁰. 522 (1934); F. MARSCHAK und D. STEPANOW, Zeits. f. Electrochem., **41**, 599 (1935); G. P. THOMPSON, Proc. Royal Soc. London, A, **125**, 352 (1929); M. C. NEUBERGER, *Die Allotropie der Chem. Elemente*, Stuttgart, 22, 23 (1936); S. B. HENDRICKS, M. E. JEFFERSON und J. F. SCHULTZ, Zeits. Kryst., **73**, 378, 379 (1930); L. VEGARD und H. DALE, *ibidem*, **67**, 157 (1928); S. VALENTINER und G. BECKER, *Naturwissenschaften*, **17**, 639 (1929); L. R. INGERSOLL und J. D. HANAWALT, Phys. Rev. **34**, 972 (1929); L. MAZZA und A. G. NASINI, Phil. Mag., **7**, 301 (1929).

[2]) E. ROSENBOHM and F. M. JAEGER, Proc. Royal Acad. Amsterdam, **39**, 372 (1936).

[3]) Idem, Proc. Royal Acad. Amsterdam, **39**, 380 (1936).

[4]) Idem, Proc. Royal Acad. Amsterdam, **39**, 477 (1936).

demonstrates that the field of stable existence of the hexagonal α'-form lies between 345° and 351° C. As the transformations $\alpha \rightleftarrows \alpha'$- and $\alpha' \rightleftarrows \beta$-*nickel* are rather *slow*, truly reproducible values of $\bar{c}_p$ for the α'-form can only be obtained, if the metal has previously been heated at the constant temperature of t° C. *during a sufficiently long time*: otherwise the values of $\bar{c}_p$, — and also of other physical properties, — evidently correspond only to more or less *in*definite "intermediate" states. In the Table the latter values are marked with an asterisk. The specific heats of the α'-modification, within its field of stability, can equally well be determined when starting with the α-, as with the β-state of the metal, — a fact which proves the truly reversible character of these transitions.

§ 2. Purest *nickel* in small lumps of pea-size[1]) was melted and then slowly cooled in the high vacuum of an induction-furnace. The mass obtained was turned off on the lathe and shaped in the form of a conus fitting within the platinum vacuum-crucibles always used in the calorimetrical work of this laboratory. The *nickel*-block weighed 44.0500 grammes, the platinum crucible 25.8848 grammes. The maximum temperature of the calorimeter-block in all experiments was reached in about 5 minutes after the crucible had been dropped into the instrument. In the beginning the solidified metal proved not yet completely to have been stabilized; but heating at 600° C. during a long time resulted in the establishment of its stabilized condition. All data obtained are collected in the following table; for the reduction Q to Q_0, as the most probable value of $\bar{c}_p$ between 20° and 0° C.: $\bar{c}_p = 0.1024$ was made use of.

§ 3. From these data we can calculate the quantities of heat Q_0 developed by 1 gramme of *nickel* between 0° and 350° C. with a fair degree of accuracy by means of the formula:

$$Q_0 = 0.10115 \,.\, t + 0.56282 \,.\, 10^{-4} \,.\, t^2 + 0.1313 \,.\, 10^{-7} \,.\, t^3.$$

The positive or negative deviations between the values observed and calculated with the aid of this formula prove to be distributed at random and never to exceed 0.5 to 2.5 pro mille; the agreement, therefore, is sufficiently accurate.

The true specific heats C_p can, within this interval of temperatures, be expressed by:

$$c_p = 0.10115 + 0.112564 \,.\, 10^{-3} \,.\, t + 0.3939 \,.\, 10^{-7} \,.\, t^2,$$

and the atomic heats C_p by:

$$C_p = 5.9356 + 0.66053 \,.\, 10^{-2} \,.\, t + 0.231142 \,.\, 10^{-5} \,.\, t^2.$$

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[1]) Furnished by Dr. FRAENKEL and Dr. LANDAU, Berlin-Oberschöneweide.

TABLE I.

Mean Specific Heats of Nickel between 0° and 1000° C.

No of the Experiment:	Temp. t in ° Cent.:	Quantity of Heat Q developed by 1 gramme of nickel between t° and t' in Calories:	Quantity of Heat Q_0 developed between t° and 0° C. in Calories:	Mean Specific Heat $\bar{c}_p$ in Calories:
60	196°.5	19.96	22.15	0.1140
56	251.2	27.02	29.17	0.1174
41	298.8	33.37	35.58	0.1203
20	299.0	33.36	35.52	0.1200
21	323.2	36.83	39.03	0.1221
42	326.0	37.21	39.43	0.1223
18	335.9	38.67	40.91	0.1231
22	340.6	39.28	41.50	0.1232
47	343.8	39.60	41.83	0.1230
48	343.8	39.75	41.98	0.1234
40	344.4	39.79	41.99	0.1233
49	344.4	39.82	42.05	0.1234
24	345.1	39.81	42.04	0.1234
50	345.1	40.14	42.33	0.1240
51	345.5	40.11	42.25	0.1236
*43	346.7	40.15	42.37	0.1236
26	346.0	40.12	42.34	0.1237
*54	346.8	40.11	42.35	0.1235
55	346.8	40.26	42.50	0.1239
*52	346.9	40.11	42.33	0.1234
25	347.6	40.39	42.59	0.1239
45	348.3	40.48	42.69	0.1239
46	348.3	40.57	42.80	0.1242
*36	348.5	40.39	42.62	0.1236
44	349.1	40.64	42.81	0.1239
37	349.4	40.60	42.83	0.1240
35	349.9	40.72	42.93	0.1240
23	349.8	40.84 (?)	43.07 (?)	0.1245
33	350.25	40.74	42.97	0.1240
*31	350.5	40.60	42.82	0.1235
32	350.8	40.78	43.01	0.1240
*30	351.3	40.83	43.02	0.1238
39	351.6	41.05	43.24	0.1243
38	352.8	41.22	43.45	0.1245
29	352.9	40.82 (?)	43.06 (?)	0.1233
28	354.8	41.30	43.53	0.1240
27	360.0	42.19	44.42	0.1248
53	383.9	45.36	47.60	0.1250
34	428.8	50.95	53.13	0.1251
17	599.5	71.18	73.44	0.1261
57	700.6	85.82	88.14	0.1266
58	804.9	99.54	101.97	0.1274
59	948.5	118.70	121.14	0.1284

The initial observations, made with the not yet stabilized metal, are omitted in this table.

Some of the values of c_p and C_p thus calculated are the following:

t:	c_p:	C_p:
100°	0.1128	6.619
150	0.1189	6.978
200	0.1252	7.349
250	0.1318	7.734
300	0.1385	8.125
345	0.1448	8.495

The increase of C_p with the temperature is remarkably steep, as can be seen from the C_p-t-curve for the α-modification graphically represented in Figure 1.

The specific heats of the α'-modification, on the other hand, can between 345° C. and 351° C. be represented by the formula:

$$c_p = 0.10321 + 0.1111 \,.\, 10^{-3} \,.\, t,$$

and its atomic heats C_p by:

$$C_p = 6.0563 + 0.65193 \,.\, 10^{-2} \,.\, t;$$

so that C_p is at 345° C.: 8.305 and at 351° C.: 8.335. (Fig. 1.)

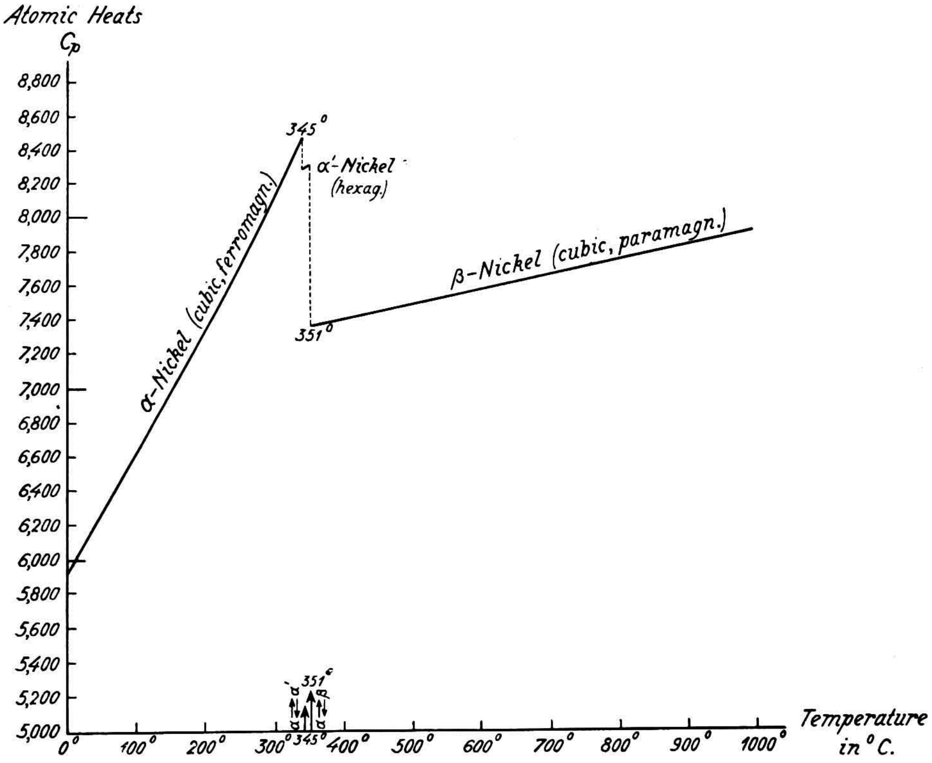

Fig. 1. *The true Atomic Heats C_p of Nickel between 0° and 1000° C.*

The specific heats of β-nickel can, between 360° and 1000° C., be represented by the formula:

$$c_p = 0.1261 + 0.1449 \,.\, 10^{-4} \, (t - 360),$$

and its atomic heats, therefore, by:

$$C_p = 7.39967 + 0.85028 \,.\, 10^{-3} \,.\, (t - 360).$$

Some of the values of c_p and C_p thus calculated, are as follows:

t:	c_p:	C_p:
360°	0.1261	7.400
400	0 1267	7.435
500	0.1281	7.517
600	0.1295	7.617
700	0.1310	7.687
800	0.1324	7.769
900	0.1339	7.857
1000	0.1354	7.945

The C_p-t-curve for *β-nickel* is simultaneously reproduced in Figure 1; evidently its slope is much less steep than in the case of the α-form.

As to the heats of transformation at the transition-temperatures, it can approximately be deduced from the previous data that the heat-effect of the transformation: $\alpha \rightleftarrows \alpha'$ at 345° C. must be of the order: 0.08 cal.; that of the transformation $\alpha' \rightleftarrows$ *β-nickel* at 351° C. of the order: 0.31 cal. pro gramme; so that he heat of transformation: α-$\rightleftarrows$ β-form is about: 0.39 calories pro gramme at 345°—350° C. —

These measurements were executed in the *Laboratory for Inorganic and Physical Chemistry* of the University of *Groningen*. I hereby wish to express my sincere thanks to Prof. Dr. F. M. JAEGER, director of the said laboratory, and to his assistants, Dr. ROSENBOHM and Dr. BOTTEMA, for their interest and their kind help during my work on this subject.

Groningen, May 1936.