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As interest is increasing in various branches of chemical production of hard absorbents, the question of obtaining the most active types is of more serious significance. Especially at the present, the question arises of obtaining absorbents which are free from the same shortcomings as the wood activated charcoal and silicagel, as they may be used in the coke-benzole production industry.

While working on the problem of obtaining hard absorbents for the purpose of capturing benzole from coke gas, we found the need for creating composite absorbents, which would be obtained principally from mined coal with added mixtures of activating and binding agents.

As with numerous other materials, we experimented with various types of clays and kaolins. They, in our opinion, had to play a given role as additive mixtures to coal. As a result of this, we found that it was necessary for us to study clays, mainly as applied to their properties that in one way or another would play a role as additive mixtures to the basic absorbents. It was especially important and interesting to study the changes of those properties depending on thermal forming, which would give indications as to the behavior of clays, while used as additive mixtures during coal activation.

These methods were used to study clay behavior in an environment of thermal activation of absorbing materials and the changes of their absorbing capacity, and were the basis for this investigation.

The ability of clay to absorb compounds of multimolecular construction from anhydrous solutions has been known for a long time, and it has been exploited for the filtration of fats and oils. Studies also have been conducted on many types of clays, as to their absorbing ability and type of application. It is worthwhile mentioning that important work in this field has been done by

Hurvych [1], Hryhoriev [2], Anteney [3], Neuman and Kober [4], Vosnesensky, Khokhrakov [5], and amny others, in order to have a proper understanding as to the degree to which research on this subject has been conducted.

However, regardless of numerous studies conducted on the "cleansing" ability of clays, the question of their absorbing ability as it applies to gases has not been studied. The study of molecular structures and their porosity characteristics has not been the subject of detailed scientific research.

We conducted a number of experiments: 1) to classify the absorbing quality of two samples of clay on benzole and water vapors with various concentrations in the air, 2) to study the absorbing capacity of clays with respect to the temperature at which previous firing was conducted, and 3) to calculate pore diameters and their general arrangement in the porosity of the absorbing material.

As samples for this study, we chose clay from Chasiv-Yarsky fields (brand R.V.), and Volodymyrivsky kaolin.

The chemical composition of the samples were [6]:

Chasiv-Yarsky clay	у %%	Volodymyrivsky kaolin	у %%
SiO_2	52,95	SiO_2	45,56
Al_2O_3	31,95	Al_2O_3	37,72
Fe_2O_3	0,91	Fe_2O_3	0,72
TiO_2	0,90	TiO_2	0,39
CaO	1,39	CaO	0,48
MgO	0,68	MgO	0,23
Loss by firing	9,30	Loss by firing	13,88

Moisture content of air dried samples was 10.34% for the Volodymyrsky kaolin, Chasiv-Yarsky clay; 13.31%.

Classification of Absorbing Activity of Clays Depending on Their Thermal Preparation

In order to obtain comparative results and to minimize the possibility of experimental errors, which are at times unavoidable with such materials as clays, we selected samples from pure and homogeneous materials, crushed them, and sifted them through a fine wire mesh containing 900 holes per square centimeter. Upon sifting the air-dried powdered material, it was compressed into tablets, which in turn were broken up into granules measuring 3 mm. Utilizing these methods, the material was prepared for final testing.

In order to study the absorbing quality of the materials as related to the thermal finishing of clay and kaolin, the selected samples were fired at temperatures ranging from 100° to 1000° C, and then were tested for absorption in benzole and water vapors.

The firing of the samples was conducted as follows: A small quantity (3 to 5 g) of sampled material was placed in a crucible and then into an electric oven that was preheated to the required temperature. The temperature of the sample was measured by means of platinum-platinumrhodium thermocouples. The thermal stability was maintained by means of "Hereus" temperature regulators. The firing was conducted on two samples at a time, and in all instances lasted two hours.

Upon completion of the firing process, the samples were placed in an extractor located over sulphate acid (monohydrate), and cooled to ambient temperature. Then they were tested for their absorbing quality.

The classification of the samples as to their absorbing ability was conducted by statistical methods described by I. M. van Bemmeln' [7]. All method, which were fired at different temperatures, were tested for absorption of benzole vapors at 15° C and 58 mm pressure (which is 2 mm less than the pressure of saturated benzole vapor at 15° C). Experiments which were conducted in vapors of low saturation were guarded against condensation which could occur during minor variations in temperature. These temperature variations were possible while conducting prolonged tests. Reliable and steady vapor pressure was obtained in all experiments by placing all samples into the extractor together with benzole diluted with nonvolatile liquid and cleaned with paraffin base oil. In order to maintain a pressure concentration of 58 mm, a 70% solution of pure, free-of-thiophene benzole in paraffin base oil was used. By such a method, the absorbing quality, or capacity, of the samples was determined as the increase in weight was established, as the result of captured vapor.

Table 2 shows the results of the absorbing capacity of Chasiv-Yarsky clay and Volodymyrivsky kaolin, fired at 100° to 1000° C, and at 15° C, of benzole vapor, 58 mm pressure concentration.

A summation of the presented results for both types of samples investigated is presented in Figure 1, where the base line shows the temperature at which the clays were fired, and the vertical line indicates percentage of activity per weight of the sample.

The shape of the curves is interesting in terms of solutions of the problems that we are pursuing, from two points of view. First, both curves characterize the behavior of clays as absorbents at their firing. Second, they visually represent the characteristic of processes which take place in the clay during their thermal manufacturing. By this method, they present an excellent

TABLE 2

Firing temperature	Activity in y %%	
	Chasiv-Yarskiy clay	Volodymyrivsky kaolin
100	5,6	5,0
200	—	5,5
300	6,7	5,9
400	6,9	6,2
500	7,7	10,2
600	6,6	5,6
700	6,2	5,3
800	4,7	4,8
900	1,7	4,3
1000	0.2	0,5

illustration, and substantiation of the facts that were observed and established by many researchers in clay composition study.

Establishing the absorbing activity of clays as directly dependent on their porosity, we are assuming that a sharp increase in activity — which appears at a clearly expressed maximum in the temperature range close to 500° C — occurs at the moment when pores are opened to their maximum. Such enrichment of the internal surfaces of clays can only take place during the process of intensive separation of gases and other fluid components. Obviously, in the first place, water is most common as such fluid in clays.

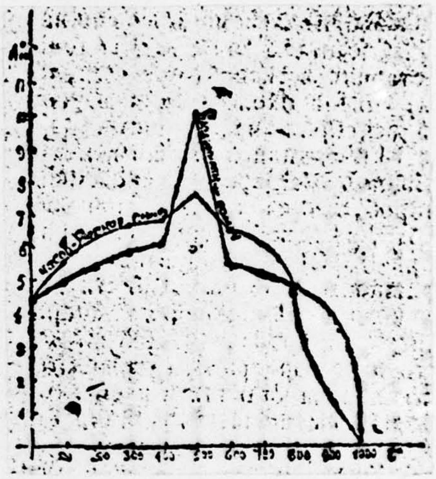

Diagram 1.
benzole, P 56 mm Hg

As other researchers, we are assuming, as Le Chatelier [8] has indicated, that water in the clay can remain by mechanical means — that is, remain there by capillary action — and by hydration, that is, having a chemical bond with the clay particles. We are assuming that the moment of maximum creation, or opening of pores, occurs during the process of dehydration.

In accordance with numerous researches conducted by such authors as I. Meellor [9], R. Ricke [10], G. Brown and E. Montomery [11], W. Kennedy [12], H. Ashley [13], and others that experimented with different types of clays, the process of dehydration of clays during their firing takes place, and intensive water separation occurs between 400° and 600° C for different samples; however, for most samples it occurs at 450° to 510° C. We are not going to elaborate on the mechanics of water separation from clays, and their chemical composition, for it would distract us from the main objective of our research. Also, due to the fact that this subject is covered in volumes of research material, we are only going to indicate that water separation at high temperatures from the internal portion of clay granules must be beneficial for a rich capillary arrangement. Surely, as a result of intensive evaporation of water from the surfaces of clay granules and the more difficult process of separation from the internal parts, the movement of water from the center to the surface takes place at different velocities, and by this action creates internal pressures that are instrumental in establishing minute fractures and pores.

Upon completion of the dehydration process, the established capillary network remains free, as a result of rigid particles of clay, and thereby becomes an excellent absorber.

A higher firing temperature of clays, as is shown in the figure, leads to a lower absorbing capacity. It appears that the lower absorption capacity is related to the change of porosity of the clay sample. It appears that with a temperature increase over 500° C on the experimental samples, some process occurs that lowers the porosity.

In accordance with speculation of A. Bleininger and Brown [14] and other authoritative researchers of clay, in the dehydration process clays lose volume, known as firing loss, and at the same time their porosity is lowered. The lower porosity is normally attributed to the baking process; however, there are other reasons that affect the porosity of clay at lower temperatures.

The samples studied by us demonstrate two abrupt changes in the reduction of porosity. The first is applicable to both samples and appears to follow the temperature of dehydration; the second is at 800° C for the Chasiv-Yarsky clay, and in the vicinity of 1000° C for the Volodymyrivsky kaolin. It is characteristic that especially sharp changes occur in the absorbing quality of kaolin that is fired at 600° C; at the same time, a loss of volume is very apparent. The second change is applicable to clays as well as to kaolin. It appears to start at the beginning of the firing process, and affects the Chasiv-Yarskiy clay before the Volodymyrivsky kaolin, which again is supported with established facts.

The results obtained demonstrate that the absorbing quality of fired clays can indicate a change of their porosity during the process of thermal finishing.

Our further research was directed toward a study of porosity characteristics - that is, the absolute appraisal of clay pores.

Isothermal Classification of Absorption

In order to establish pore sizes in fired clay that are helpful in grading the suitability of abosrbents, we conducted a number of required experiments that provided us with the necessary material to make calculations. In order to calculate the absolute size of the pores, we needed, as will be shown in the text, to obtain a number of isothermal curves of absorption of various vapors on different samples of clay. We limited our experiments to the isothermal curve of absorption of water and benzole vapors on Chasiv-Yarsky clay that was fired at 500° C.

In order to establish the isothermal curve of absorption, we exploited the statistical method of J. M. Bemmeln [15], as it was most appropriate for our conditions. For both the water and benzole vapors, we took six readings of vapor pressure at various levels. The given vapor pressures were obtained over the material by placing into an extractor a box or crystallizer with a proper mixture of benzole with paraffin base oil, or water with sulfate acid, and in both cases, clay. In obtaining the required mixtures, we used the data given by W. Bachmann [16], shown in Table 3.

TABLE 3. At 15° C

Water-sulfate acid		Benzole-paraffin base oil	
% sulfate acid	Vapor pressure, mm	% benzole	Vapor pressure, mm
71,50	0,85	3,00	10,00
51,00	4,20	7,50	20,00
42,50	6,55	14,00	30,00
34,15	8,77	24,00	40,00
24,80	10,55	40,00	50,00
0,00	12,70	70,00	58,00
—	—	100,00	60,00

The points of the isothermal curve were established as a weight increase in % when equilibrium was reached. It is important to mention that the equilibrium was achieved at a very slow pace; in some cases it took 7 to 10 days, after which time no practical change was noticed.

Table 4 represents results of measurements obtained of the isothermal curve of water vapor (1st column) and benzole vapor (3rd column) on absorption by Chasiv-Yarsky clay at 15° C. In this example, the measurements were conducted as follows: several samples of fired clay, right after cooling to ambient temperature, were placed into separate extractors with specific vapor at given vapor pressure; then, after equilibrium was reached, they were weighed.

TABLE 4

For benzole		For water	
P, mm	Activity, %	P, mm	Activity, %
10	1,0	0,85	0,47
20	1,6	4,20	1,48
30	2,2	6,55	2,34
40	2,5	8,77	4,39
50	2,9	10,55	5,76
58	6,4	12,70	18,50
60	18,0	—	—

In order to achieve a higher confidence level in our results, we separately repeated our experiments, while changing them in many ways. For example, we took several measurements while using the same sample and subjecting it each time to a higher vapor pressure, after equilibrium was achieved at the next lower pressure. With this type of testing, no appreciable change in weight was noticed.

Other experiments than those described above were conducted using the analogy of R. Zsigmondy [17] of flooding and deflooding of jellies.

Assuming a widening of isothermal curves that represents absorption and de-absorption of benzole vapors in clay, we conducted the following experiment. We took samples of Chasiv-Yarsky clay, prepared as for the previous experiments, subjected them to firing for two hours at 500° C, and then cooled them in an extractor over phosphate-anhydride. The samples were in tablet form, previously weighed, and placed into flask "A", shown in Figure 1, by means of a wire spoon. Flask "A" with a tight stopper was connected from one side by valve K with retort B filled with pure benzole. From the other side, it was connected to a Pfeifer flask. In order to assure maximum flow of molecules of the material to be absorbed to the smallest pores of the absorber, and as much as possible to eliminate the occurrence of air locks that normally slow the flow of vapors in capillary pores, flask A with its clay sample was evacuated.

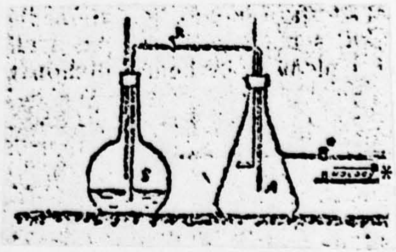

Figure 1
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Then, while the Pfeifer flask was continuously active, we operated valve K to allow benzole to flow to flask A in small drops. Each drop of benzole upon entry was expended, then froze to take the shape of snow flakes, and fell to the bottom of the flask. By this method, we achieved proof that the absorber achieved equilibrium with benzole vapors of low pressure, and filled the larger capillaries. When by means of the regulating valve the flow of benzole was increased, the vapor pressure in flask A also started to increase. This allowed for more capillaries to be filled. And finally, benzole was preheated to 50° C, and was allowed into flask A, where it was brought to boiling by lowering of the vacuum. Upon the boiling process in the flask, and removal of the vacuum, the samples were transferred into liquid benzole, where they were subjected to boiling again, this time at atmospheric pressure. After benzole was cooled to 15° C, the samples were removed, and upon disappearance of visible remains of benzole (which took 1 second) the samples were placed in weighing jars and weighed. The weight results showed an excellent increase as compared to earlier obtained data from experiments in saturated vapor by using the I. Van Bemmeln method. Three samples resulted in 17.90%, 18.05%, and 18.03%, which can be assumed to be correct as 18.0% was previously established. The obtained data were used as a starting point for the isothermal curve of benzole de-absorption, which corresponds to saturated vapor.

Then we continued our research based on the fact that we were transferring samples, after they reached equilibrium in the extractors with higher benzole vapor pressure, to extractors with lower vapor pressure. By such a method, we created a reverse path on the isothermal curve of benzole vapor absorption by Chasiv-Yarsky clay.

Diagram 2 shows results compiled during research to establish the isothermal curve of absorption of water (the upper solid curve), benzole vapor (lower solid curve), and the isothermal curve of de-absorption of benzole vapor (broken curve), using Chasiv-Yarsky clay fired at 500° C, and used at 15° C. For simplicity of comparison, the curves to determine saturation of the absorbing material are read on vertical lines, and saturation of vapors to be absorbed are read on horizontal lines. The vertical ordinate shows the relationship of absorbed quantity V to the whole quantity absorbed of saturated vapor V_s; the horizontal line shows the relation of vapor pressure P to vapor pressure of saturated vapor P_s.

When we analyze the curves of absorption, first we notice the sharp deviation in curve characteristic of absorption at a point where $P/P_s = 0.5$, and after it. The first halves of the isothermal curves are nearly together for both vapors. They rise smoothly to a given limit, then they reach a starting point of the second half where $P/P_s = 0.5$, and they then acquire a tendency to rise at a sharper rate. The rise of the benzole vapor curve is slower; at P/P_s it equals approximately 0.5. The curve representing water vapor has two bends — the first is smooth and directed lower at

$P/P_s = 0.5$, and the second is much sharper where $P/P_s = 0.8$, where it meets with the sharp bend of the benzole vapor curve.

This type of absorption characteristic is easy to explain, when we make a definite assumption that the absorption of vapors by hard, porous absorbers consists of two processes: absorption where P/P_s equals a small value, and capillary condensation where P/P_s approaches a value of one.

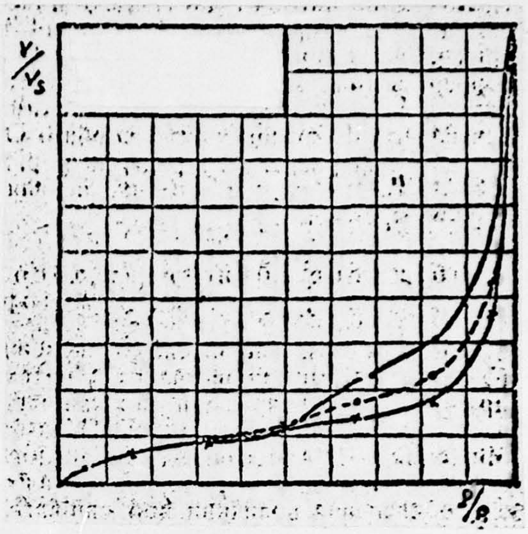

Diagram 2

—·— water ··•·· benzole desorption
—×— benzole/absorption

Another condition that attracts attention appears from a detailed study of Diagram 2 is the very pronounced hysteresis of the absorption and desorption curve for the benzole vapors. This phenomenon was observed by other authors, such as I. van Bemmeln [18], I. Anderson [19], I. McGavack and Patrick [20], and others. The first to explain it was R. Zsigmondy [21]. He defined it as a slowing of the moisturizing process of the capillary walls with condensed vapor by captured absorbing air. It is a fact that by complete dehydration of the absorbing material the area represented by hysteresis can be reduced or totally disappear, as was demonstrated by I McGavack and Patrick [22] on the example of absorption of sulfate gas by silicagel.

There are authors who take Zsigmondy's definition of the hysteresis under discussion, and feel that the reason for the rise in the desorption curve is evaporation of absorbed material from the finer capillaries. However, we tend to agree with Zsygmondy, and therefore we take the real curve representing absorption. We will take more data required for calculation of pore radii from the isothermal absorption curve for benzole, represented with dots and dashes on Diagram 2.

Approximate Calculation of Absolute Value of Pore Radius

In order to make an approximate calculation of the absolute value of pore radii, we exploited the mathematical relation between the pressure of saturated vapor over the capillary and its radius. This relationship first was established by W. Thomson [23]. By using other means, Minkowski [24] and I. Anderson [25] proved that vapors that are not included in the Clapyron equation can be used for pore size calculations in silicagel.

According to I. Anderson:

$$r = \frac{2\sigma\rho_s}{\rho P_s \ln\frac{P_s}{P}}$$

where r — average radius of miniscus curvature; σ — liquid surface tension; ρ_c — density of saturated vapor; ρ — density of liquid; P_s — vapor pressure of saturated vapor in mm Hg; and P — vapor pressure on the capillary meniscus.

We assume that, in a state of equilibrium between the absorbing material and vapor from the material to be absorbed, the vapor pressure in the capillary must equal the vapor pressure over the surface of the absorbing material. We can then conclude that for each given vapor pressure of the material to be absorbed, in the process of capillary condensation, filling will occur with a liquid capillary having a radius for which the vapor pressure over the meniscus equals the vapor pressure over the liquid itself. Therefore, each point on the isothermal curve of absorption corresponds to filling of only capillaries of the absorber over which the vapor pressure equals the vapor pressure over the full capillaries with larger radii. Then in this case condensation in these capillaries cannot take place. It will take place only when the vapor pressure of the material being absorbed increases to a point equal to the vapor pressure corresponding to the pressure in the capillary of a given radius. This means that by increasing vapor pressure of the material being absorbed, condensation will gradually take place in the wider capillaries. Then the flow of the isothermal curve characterizes the order in which the capillaries will be filled according to the increase in size of their radii.

Table 5 shows the relationship of vapor pressure over the capillary meniscus radii, calculated in accordance with Anderson's equation for water and benzole vapors at 15° C.

Making use of this table and the isothermal absorption curve for benzole, the radius of capillaries that take part in absorption by a given vapor pressure can be determined. Also, the porosity of the material can be determined, which is covered by capillaries of various sizes. Determination of the predominant radius of pores in the absorber pores can also be achieved. In short, a differential can be constructed to show the distribution of pores by size, in the volume of the absorber.

By scaling the vertical line in relation to volume filled at a given vapor pressure to logarithms of pore diameter [$V/(V_s/\lg D)$] and by scaling the horizontal line with logarithms of pore diameters, as was done by P. Kubelka [26], we obtained a structural curve for the Chasiv-Yarksy clay, fired at 500° C (Diagram 3). The obtained structural curve first of all attracts attention due to its simplicity, which indicates that the distribution of pore

TABLE 5

Water P_s = 12.7 mm		Benzole P_s = 60 mm	
P_{mm}	$r\,m\mu$	P_{mm}	$r\,m\mu$
1,0	0,35	6,0	0,94
4,0	0,95	10,0	1,21
5,0	1,18	12,0	1,35
5,5	1,31	14,0	1,49
6,0	1,47	16,0	1,64
7,0	1,85	20,0	1,97
8,0	2,38	22,0	2,16
9,0	3,20	26,0	2,60
10,0	4,61	30,0	3,13
11,0	7,69	32,0	3,45
11,5	11,11	40,0	5,36
12,0	19,46	48,0	9,73
12,5	69,39	56,0	31,49
12,7	—	60,0	—

sizes in the porosity of our sample is even. Where the radii of pores are 1 mμ to 3 mμ , the curve is almost parallel to the diameter of the pores, until it approaches the smallest pores. When it reaches the size of pores that will allow entry of the molecules of benzole only, then it begins to fall. A gentle down-slope is also observed in the area of the largest pores, which is normal for naturally porous bodies.

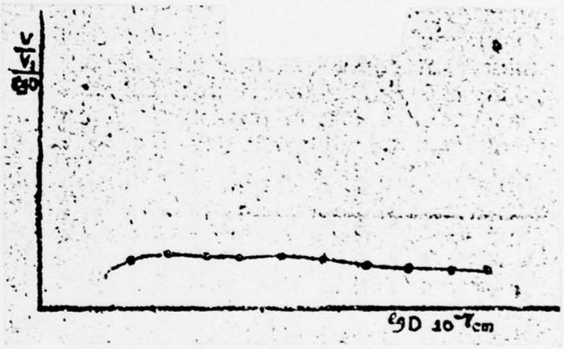

Diagram 3.

The practical results obtained by us as to the characteristics of pores for fired Chasiv-Yarsky clay led us to evaluate it as an absorbing material. First, for use as an absorber from the gaseous state in the area of small concentrations, the sample studied by us does not arouse interest for use, because its structural arrangement curve does not have a clear maximum in the area of minute porosity. Second, for use as a binding agent, the clay did not fail to attract interest and can play a role as a skeleton for separation of active forms of carbon in the process of coal activation.

This report discusses the results of the following research:

Resume

1. We researched the absorbing capacity of benzole by Chasiv-Yarskiy clay and Volodymyrivsky kaolin with respect to their firing temperatures;

2. We studied the isothermal curve of absorption of benzole and water vapors by Chasiv-Yarsky clay fired at 500° C,

3. We calculated the absolute pore sizes and ~~plotte~~d the structural curve for Chasiv-Yarskiy clay fired at 500° C;

4. We made practical conclusions regarding clay as an absorber of gases, and as a binding agent in the production of granular activated coal were made.

REFERENCES

1 Научные основы переработки нефти (*1921*).
2 Ж. Хим. Пром., 2, 731 (*1926*).
3 Ind. Chimique, 14, 192 (*1927*).
4 Zt. f. angew. Ch., 40, 337 (*1927*).
5 Ж. Пр. Хим., 2, 633 (*1930*).
6 Труды Ц. Лаб. Укр. Огнеуп. Цем. Треста под ред. проф. П. П. Будникова.
7 Zt. f. anorg. Ch, 13, 234 (*1896*).
8 Zt. f. phys. Ch., I, 396 (*1887*).
9 Trans. Cer. Soc. (Eng.) X, 94.
10 Sprechsaal, XLIV 637, 653 (*1911*).
11 U. S. Bur. of Stand. Tech. Pap., 21 (*1912*).
12 Trans. Am. Cer. Soc., IV, 152 (*1902*).
13 Jour. Ind. and Chem. Eng., III, 91 (*1910*).
14 U. S. Bur. Stand. Bull., 7, 22.
15 l. c.
16 Zt. f. anorg. Ch., 100 (*1917*).
17 Zt. f. anorg. Ch., 71, 356 (*1911*)
18 l. c.
19 Zt. f. phys. Ch., 88, 191 (*1914*).
20 Journ. Am. Chem. Soc., 42, 946 (*1920*)
21 l. c.
22 l. c.
23 Phyl. Mag., 42, 448 (*1871*).
24 Enzykl. der math. Wiss., 4, 571 (*1907*).
25 Zt. f. phys. Ch, 88, 191 (*1914*).