

SOME COMMENTS ON THEORIES CONCERNING THE CONNECTIONS BETWEEN TRUE (BULK) ABSORPTION AND DIFFUSE REFLECTANCE SPECTRA OF POWDERED SOLIDS

Part I. On Bodó's theory

By

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(Received May 10, 1970)

The purpose of this work was to study in detail the characteristic features of different theories on the connections between the true (bulk) absorption and diffuse reflectance spectra, with special regard to the role of the parameters used. On this behalf, the functions $R_{\infty} = R_{\infty}(kl)$ were calculated on the basis of the most important theories and the numerical data obtained were analysed with graphical methods. The results of the analysis give useful information from metrological points of view, and, on the other hand, may serve as a useful guide for further experimental work.

The present paper, after an introduction giving a short review of the problems with regard to the sources of errors, deals chiefly with Bodó's theory; considerations on other theories are to be treated in subsequent papers.

Introduction

Researches on the optical properties of powdered solids are of special interest both from a purely scientific and from an industrial point of view. Though numerous investigations in this field have been made in the last two decades, a satisfactory settling of emerging problems or at least promising perspectives for their solution are still to be expected. Researches yielding quantitative results are relatively few and most of the models describing the propagation of radiation in powdered disperse media do not seem to have been elaborated with regard to all possible consequences.

Here we have in mind, in the first place, the models leading to an estimate for the absorption coefficient, such as those used in Bodó's [1], [2], Johnson's [3], Antonov-Romanovsky's [4] Girin and Stepanov's [5] and Melamed's [6] theories. It is indiscutable that the problem is very complex and difficult to approach; nevertheless we think that the available theories still offer possibilities which have not been fully exhausted. Namely, to our knowledge, neither of the six models published in the last fifteen years had been subjected to detailed and extensive theoretical and experimental examinations; only Bodó attempted, in some later publications [7], [8], at studying the structure of powder layers. Thus not only a deeper analysis of some models seems to be wanting but we also have to dispense with comparative

researches concerning their mutual connections. It was only recently that results aiming at a partial filling of this gap were published [9], [10], [11].

In the last years systematical researches were begun in our institute, in order to elucidate the connections between the different theories, their limits of validity, the possibilities of their application and, last but not least, to find the most expedient ways of further development. An account of the first results was given in some papers [11], [12], [3], and further contributions to this problem shall be published shortly.

The problems to be discussed

On the basis of our foregoing results [10—13] and in view of a more detailed approach to the problems, it seemed necessary to examine more exactly which of the models would appear as best founded from a physical point of view, which model would offer perspectives for essential development and in what directions further theoretical and experimental investigations were to be made.

In this and some following articles we wish to examine theoretically the efficiency of the different theories (models) and the effects of the parameters used by different authors (refractive index, reflection coefficient, absorption coefficient and particle size i.e. optical thickness of the powder particles) on diffuse reflectance spectra.

Considering that one of the objects of diffuse reflectance spectroscopy is to determine the true (bulk) absorption coefficient from the diffuse reflectance spectrum of the powder sample, it has to be examined in what degree the errors of measurements will influence the calculated absorption coefficient. As it is difficult to assess the character, importance, magnitude and effect of the different sources of error, it will be necessary to give a short review of the most important points from which they may result.

- a) Systematical errors of the equipments (only approximative exactness of geometry, approximate validity of principles of measurement etc.) can be reduced by relative methods of measurement or by an adequate calibration curve. This is why diffuse reflectance measurements are generally made with relative methods, involving one of the most important sources of error, namely, the irreproducibility and instability (ageing etc.) of the reference standards. One of the most essential and uncontrollable errors in determining the absolute diffuse reflectance seems to be due to the use of data concerning diffuse reflectance of the reference standard to be found in literature. It is well known that the data for absolute diffuse reflectance of smoked MgO , generally used as reference standard, may differ by some percents in the publications of different authors [14—19]. In the ultra-violet region this uncertainty is increased by the dependence of the reflectance of smoked MgO standards on their preceding history [17]. Because of the difficulties mentioned above, the errors in the diffuse reflectance of reference standards may amount to 1—2% in the optimal case, and will be even greater in the ultra-violet. This can be expected to increase the uncertainty of further data (e.g. R_∞).
- b) There exist no well defined methods for preparing the samples, with the exigence of minimizing the errors due to the preparation [10, 13]. Consequently, the reproducibility of the samples used for measurements is relatively low, which may be the source of a further uncertainty of 1—2%.

c) The optimal conditions for applying different theories are not fully cleared up; so we do not dispose of the means necessary for minimizing the errors ensuing from the circumstances mentioned above under a) and b) by choosing an adequate method.

In the present paper we wish to deal first with a detailed analysis of BODÓ's theory. Similar considerations concerning other theories are to be published subsequently.

In BODÓ's theory [1, 2] the reflectance R_∞ of a powder layer of infinite thickness and the optical parameters of material of the powder are connected by the relation

$$R_\infty = \frac{1 + R_1^2 - T_1^2}{2R_1} - \sqrt{\left(\frac{1 + R_1^2 - T_1^2}{2R_1}\right)^2 - 1}, \quad (1)$$

where

$$R_1 = \frac{r[1 + (1 - 2r) \cdot \exp(-2kl)]}{1 - r^2 \cdot \exp(-2kl)}, \quad (2)$$

and

$$T_1 = \frac{(1 - r)^2 \cdot \exp(-kl)}{1 - r^2 \cdot \exp(-2kl)}, \quad (3)$$

are the reflectance and the transmission of a thin powder layer of the thickness of a single particle. Here r means the surface reflection coefficient of the thin powder layer, k the absorption coefficient of the material, and l particle size. We wish now to discuss the relations (1) to (3) in more detail. To this purpose we have computed the functions $R_\infty = R_\infty(r, kl)$, $R_1 = R_1(r, kl)$ and $T_1 = T_1(r, kl)$ for values of r most important for solids¹, i.e. for $0,017 \leq r < 0,25$, between the limits $10^{-5} \leq kl \leq 10$. A graphical analysis of the numerical data permitted to draw important conclusions.

As shown in an earlier paper [11] the one-particle models differ essentially in the way for deriving R_1 and T_1 , suggested by different authors. Because of the important influence of R_1 and T_1 on the value of R_∞ , and in order to allow a comparison of the assumptions of different authors for these parameters, we give here a short review of the connections and characteristic features of R_1 and T_1 .

As shown in Fig. 1 and Fig. 2, both R_1 and T_1 are rigorously monotonous decreasing functions of the optical thickness. Both curves have asymptotes, namely

$$R_1 = \frac{2r}{1-r} \quad \text{for } kl \rightarrow 0 \quad \text{and} \quad R_1 = r \quad \text{for } kl \rightarrow \infty;$$

similarly

$$T_1 = \frac{1-r}{1+r} \quad \text{for } kl \rightarrow 0 \quad \text{and} \quad T_1 = 0 \quad \text{for } kl \rightarrow \infty.$$

As can be seen from the figure, the dependence of R_∞ on kl is only significant in the interval $10^{-2} \leq kl \leq 1,6$, whereas T_1 significantly depends on kl for $4 \cdot 10^{-3} \leq$

¹ If the parameter r is defined by the relation $r = [(n-1)/(n+1)]^2$, as suggested by ANTONOV-ROMANOVSKY for certain cases, then our considerations will hold for refractive indices $1,3 \leq n < 3$, i.e. for most of the values found in practice.

$\cong kl \cong 4$. The course of the functions R_1 and T_1 presents the essential difference that, with increasing optical thickness T_1 becomes more and more insensitive to changes in the reflection coefficient r (or in the refractive index n), so much that for $kl \cong 4$ the T_1 curves calculated with different reflection coefficients (or refractive indices)

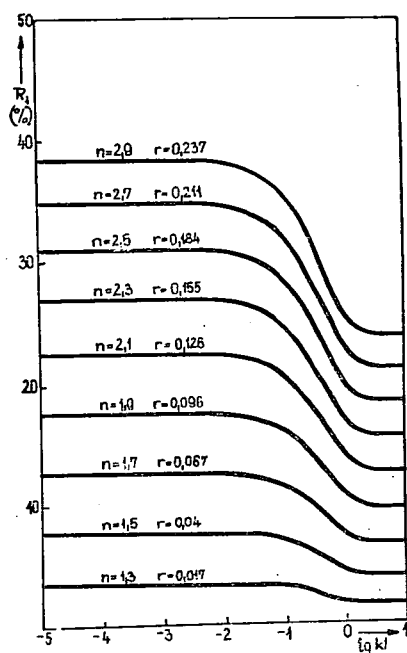


Fig. 1

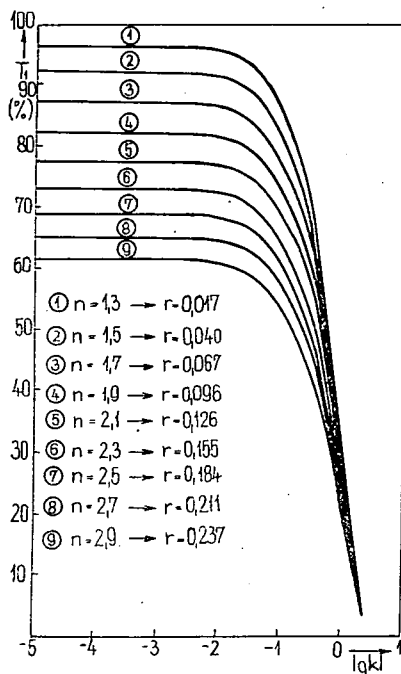


Fig. 2

practically coincide (the resolution of the curves in the diagram cannot be improved even by magnifying this region twenty times), whereas the R_1 curves are well separated for all values of kl .

It is evident from Eqs. (2) and (3) that R_1 and T_1 cannot change independently from each other; there exists a well defined connection between them, which depends only on r (or n), though the analytical form of the function $R_1 = R_1(r, T_1)$ results to be very complicated. However, as it is to see from a graphical plot of this function (Fig. 3) $R_1 = R_1(r, T_1)$ is rigorously monotonous function of T_1 , its course being strongly influenced by r (or n). The points determined by values T_1 and R_1 corresponding to identical values of kl are situated on straight lines in case of low optical thicknesses; for higher values of kl the lines become slightly concave from the right. This shows that for $kl = \text{const.}$, R_1 increases linearly or near linearly with increasing T_1 .

Now, in case of relatively great values of kl (> 0.2), most of the radiation incident on a powder layer considered as of infinite thickness will be absorbed in the uppermost powder layers and thus the role of these layers becomes dominant. This emphasizes the importance of the structure of the surface layers, studied by BODÓ and HANGOS [8]. On the other hand, for $kl > 1 \cdot 10^{-4}$ the accuracy of kl cal-

culated from R_∞ will essentially depend on r (see Eqs. (1) to (3)). The method of determining r suggested by BODÓ is, however, to be considered as problematical from the point of view of metrology. The uncertainty in the measurement of low reflectance is relatively great, and the possibility of fulfilling the condition $kl > 1,6$

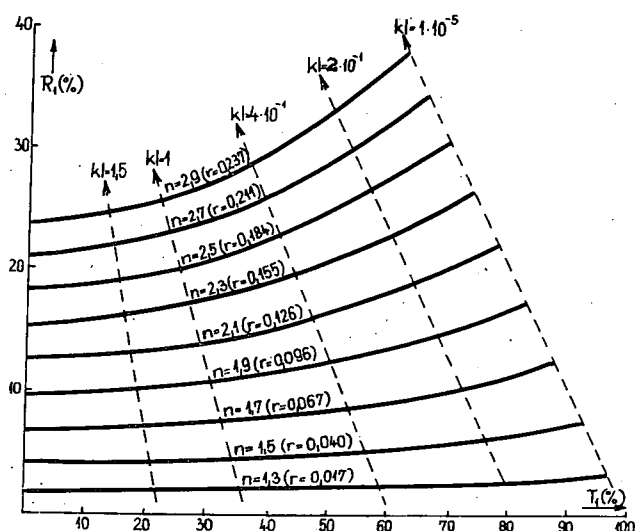


Fig. 3

seems not to be secured in every case. In view of the problems mentioned above and because the optical behaviour of powder layers of finite thickness (e.g. the validity of BODÓ's suppositions for such layers) has not been sufficiently studied, it seems not only useful but also necessary to make further optical investigations on thin powder layers.

The common aim of the theories [1, 2, 3, 4, 5, 6] being the determination of kl (or of k) from the diffuse reflectance R_∞ of a powder layer of infinite thickness, it is necessary to discuss the relation $R_\infty = R_\infty(r, kl)$. The functions $R_\infty = R_\infty(r, kl)$ calculated for different constant values of the parameter r between the limits mentioned above are plotted in Fig. 4 (in view of the wide limits set for kl in our calculations, the abscissa has been plotted on a logarithmical scale). The functions $R_\infty = R_\infty(r, \lg kl)$ are rigorously monotonous functions of $\lg kl$ (and thus of kl), which also have two asymptotes, namely

$$R_\infty = 1 \quad \text{for} \quad kl \rightarrow 0, \quad \text{and} \quad R_\infty = r \quad \text{for} \quad kl \rightarrow \infty.$$

It can be seen from the foregoing and from Fig. 4 that, for $kl \leq 1,6$, we must practically give up estimating the absorption coefficient on the basis of BODÓ's theory, independently from the value of r (or n). The determination of kl has to be restricted to the range of $kl \leq 1,6$. It follows from the course of the curves, that the

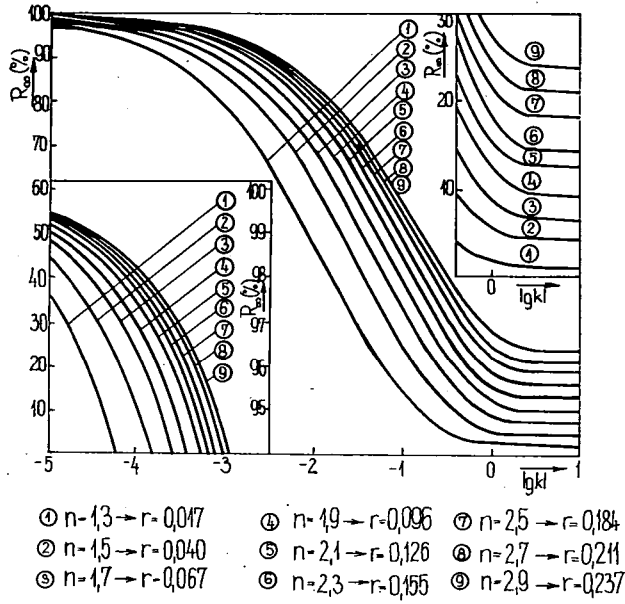


Fig. 4

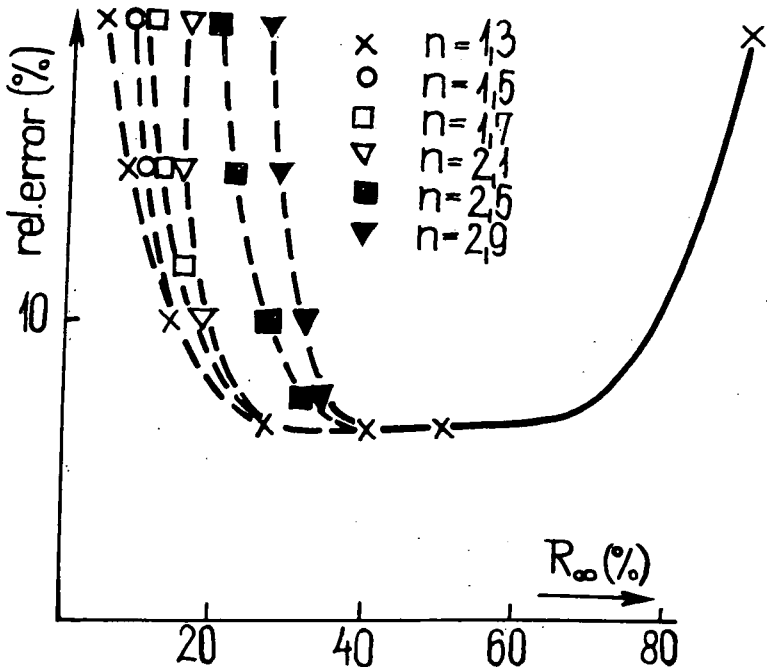


Fig. 5

accuracy of kl for constant values of the parameter r (or n) strongly depends on R_∞ (or on kl). In order to assess the error to be expected, the functions

$$F(R_\infty, r) = \frac{d(\lg kl)}{dR_\infty} \quad \text{and} \quad F(R_\infty, n) = \frac{d(\lg kl)}{dR_\infty}$$

were determined by differentiating the curves of Fig. 4 with a graphical method. The results are shown in Figs. 5 and 6. As could be expected from Fig. 4, the section in which the dependence of R_∞ on $\lg kl$ is linear will be the most favourable from a metrological point of view. This

means that this is the section in which the uncertainty due to errors of measurement will exert the least influence on the values of kl . The branches of the curves left and right of this section (corresponding to sections II and IV in Fig. 4) show an extremely steep rise, therefore the errors caused by inaccurate measurements will have a very strong influence on the values of kl , and thus the reliability of the estimate of kl suddenly decreases in case of particles of relatively high or relatively low optical thickness. The optimal range of measurements in which an error of 1% in the diffuse reflectance R_∞ causes a maximum

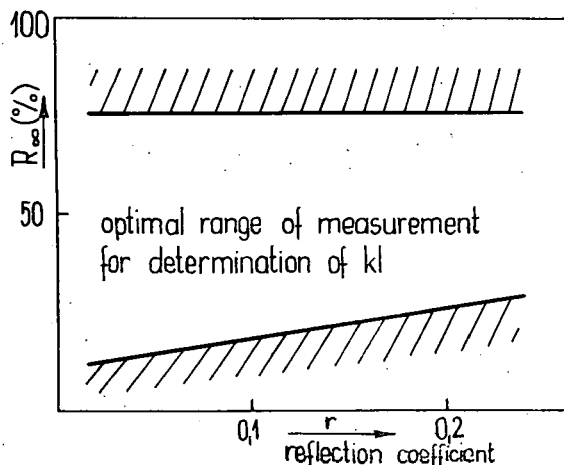


Fig. 6

relative deviation of 8% in kl is shown in Fig. 7 for different values of the reflection coefficient r or of the refractive index n). It can be seen from the figure that, with increasing r (or n), more accurate values of kl can be expected for relatively higher absorption (i.e. for less diffuse reflectance R_∞), whereas in case of lower values of r , estimates of kl for relatively low values of k can be made.

It follows from the above that it is justified to examine the importance, the role and requirements to the accuracy of the parameter r (or n) on the basis of detailed numerical calculations. It is comparatively easy to assess the situation from Fig. 8 in which the diffuse reflectance R_∞ is plotted as a function of r and n , for different constant values of kl .

A striking feature of these curves is the close dependence of their course on the value of kl . If kl is comparatively small, then, in case of refractive indices $n \geq 1.8$ (i.e. reflection coefficients $r > 0.1$) the curves $R_\infty = R_\infty(n, kl)$ for constant values of kl are straight lines nearly parallel to the abscissa, that is, the refractive index (and so the reflection coefficient) will be, in principle, without considerable influence on the diffuse reflectance, provided the diffuse reflectance is relatively high or the optical thickness sufficiently low.

In the region of relatively low refractive indices $n < 1.8$, the role of the refractive index may become more important even for low values of kl , but in the practice of solid state physics such conditions are generally rare.

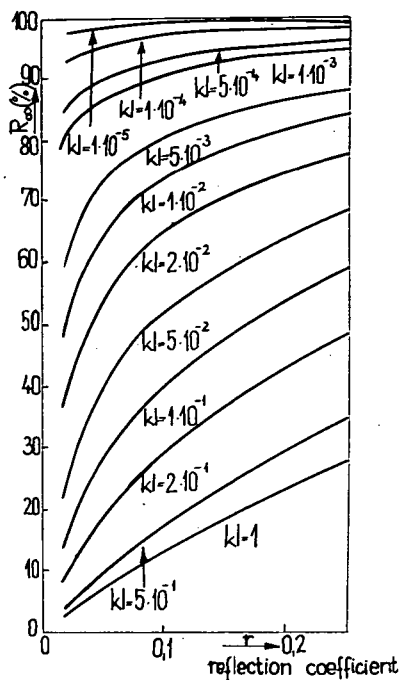


Fig. 7

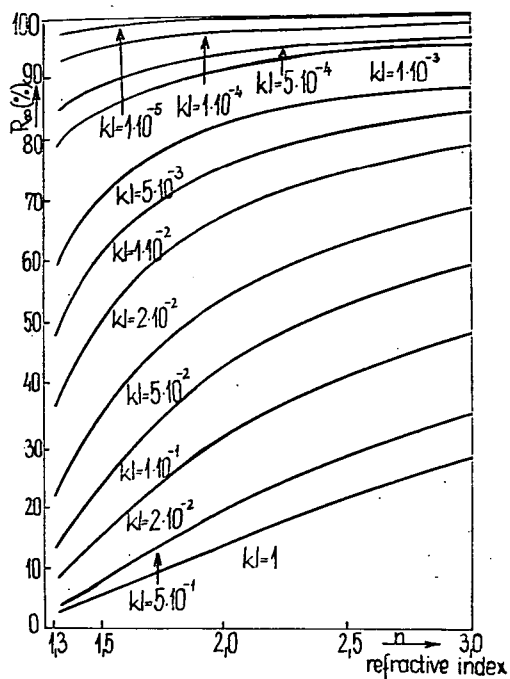


Fig. 8

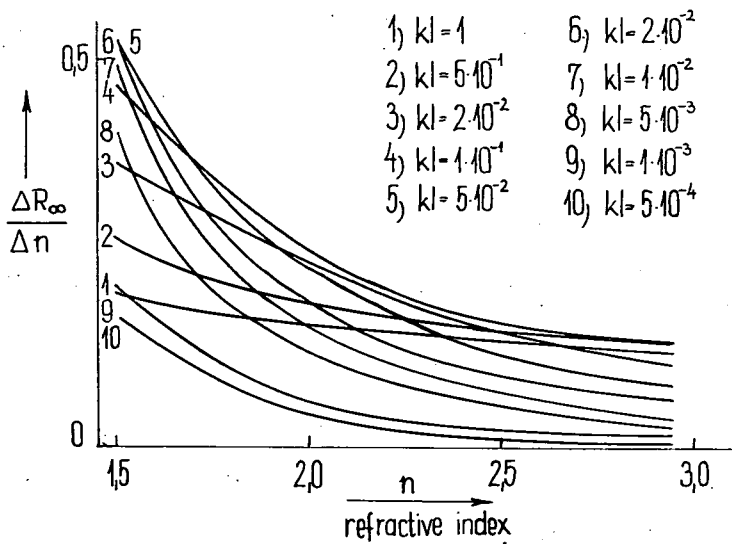


Fig. 9

With increasing optical thickness the functions $R_\infty = R_\infty(r)$ and $R_\infty = R_\infty(n)$ calculated for different constant values of kl , become steeper and steeper, first for lower, then also for higher refractive indices. In extreme cases, as for $kl=1$ the character of the curves also changes, namely, the curves originally concave from below have a point of inflection and gradually become convex from below for higher values of r or n . It results from this changing character of the curves that the influence of the refractive index on the diffuse reflectance spectra cannot be neglected for powders consisting of particles of a certain optical thickness ($kl < 10^{-5}$), and special care is necessary to eliminate the influence of the refractive index in calculating e.g. kl etc. Some orientation for a numerical evaluation of this effect can be found in Figs. 9 and 10, in which the functions $dR_\infty/dn = f(n, kl)$ and $dR_\infty/dn = f(R_\infty)$ are plotted for different constant values of kl . Quite similar curves can be obtained concerning the reflection coefficient r : namely, as it is to easy to see,

$$\frac{dR_\infty}{dr} = \frac{dR_\infty}{dn} \cdot \frac{(n+1)^3}{4(n-1)},$$

which shows that R_∞ reacts to changes in r in the same way as for n , but in consequence of

$$\frac{(n+1)^3}{4(n-1)} > 1,$$

R_∞ is, in principle, much more sensitive to changes in r . This is why it seemed preferable to use the refractive index in our present considerations.

With the aid of Fig. 10 it is possible to determine the optimal ranges of measurements of R_∞ which permit to minimize the errors due to inaccuracies of r or n . According to the figure, the range 30 to 70% results to be most favourable; this, however, overlaps only partly the region $0,25 \leq R_\infty \leq 0,75$ considered as optimal in previous paragraphs. It is evident that the most favourable conditions of measurements, from which results most correct in principle can be expected, are to be found in the section common to both ranges of R_∞ mentioned above, or in their immediate neighbourhood. This also warrants that the more or less inevitable inaccuracies of different kind will be of least influence on the reliability of the values of kl or k .

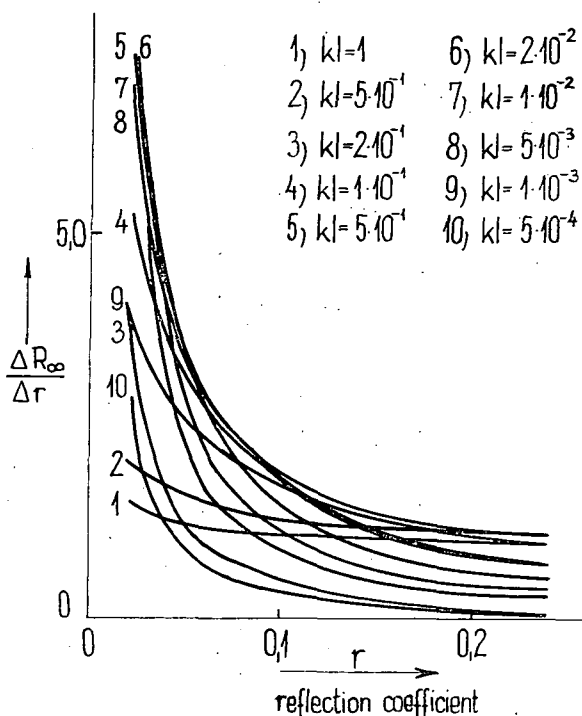


Fig. 10

Further conclusions

Though we are fully aware that BODÓ's conception is only of approximate validity and further careful experimental work is required to refine BODÓ's model, the available experimental results seem to justify the assertion that this theory gives a true picture of the essential features of the optical behaviour of powdered solids. The above conclusions allow also more precise interpretation of certain experimental results.

We wish mainly to point out two problems. BODÓ attributed the good agreement between his theoretical and experimental results to the mutual compensation of errors arising from approximation. In our opinion, this agreement is due not only to compensation of errors but also to a favourable position of the absorption band. Namely, BODÓ determined the value of r in the ultra-violet spectral region, where the absorption was sufficiently high ($kl \rightarrow \infty$) both for glass powder and luminescent powder. The spectral position of the absorption band of interest for BODÓ was not far from the point where r was measured. Consequently, supposing normal dispersion, there were no important changes in the values of r and n , and thus he could obtain a good estimate for the relatively high absorption. As mentioned above, in case of low absorption R_∞ and thus kl is practically independent from r and n , and therefore the uncertainty arising from the possible spectral dependence of r will not be of significant influence on kl or k . — Measurements to study these situations on model substances with appropriate absorption characteristics are in course, with the purpose of throwing further light on the role of the parameters r and n .

KORTÜM *et al.* [19] were the first to observe that the absorption spectrum calculated from diffuse reflectance flattens out in the ultra-violet spectral region. A similar flattening out of the spectrum was found in our calculations made on the basis of BODÓ's theory [11], using the mean refractive index for determining r . Though the calculations of KORTÜM *et al.* were founded on the theories of KUBELKA and MUNK rather than on BODÓ's model, the results obtained with the latter model may serve to elucidate the causes of the flattening of this spectrum.

As can be seen from Fig. 8, R_∞ increases with increasing r (or n) for any constant optical thickness kl . This means that, in case of normal dispersion, the reflectance spectrum will show a more or less rising tendency towards shorter wavelengths, even supposing spectral constancy of absorption in this region; i.e. the absorptivity seems to decrease in this direction ("bleaching effect"). Thus, proceeding towards shorter wavelengths, the increase in the refractive index alone is sufficient to produce decreasing absorption, which leads to the flattening out of the absorption spectrum.

The effect of the reflection coefficient r (and of the refractive index n) on the diffuse reflectance spectra can be controlled by using adequate immersion liquids, i.e. by imbedding the powder sample in a liquid which is colourless in the spectral region to be examined. By this means it will be possible to reduce the influence of the refractive index, and thus to study the finer structure of the absorption spectrum, especially in the region of low absorption. However, the influence of the immersion liquid on the diffuse reflectance spectra is theoretically asymmetrical in the sense that the range of lower absorption in the spectrum will appear comparatively accentuated against the regions of higher absorption. Thus, investigations with the use of

immersion liquids can be expected to give valuable contributions concerning the mechanism of propagation of radiation in powdered (or, generally, disperse) media.

Finally we wish to remark that the independence of R_{∞} from the refractive index helps to understand the constancy of the diffuse reflectance of reference standards in the spectral region of very weak absorption, in spite of the dispersion of the refractive index.

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The author is indebted to Prof. I. KETSKEMETY, director of the Institute for his kind interest and valuable remarks.

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ЗАМЕТКИ К ТЕОРИЯМ ОТНОСЯЩИМСЯ К СВЯЗИ МЕЖДУ СПЕКТРАМИ ИСТИННОГО (МАССИВНОГО) ПОГЛОЩЕНИЯ И ДИФFUЗНОГО ОТРАЖЕНИЯ ПОРОШКООБРАЗНЫХ ТВЁРДЫХ ВЕЩЕСТВ

Б. Карвай

Целью данной работой и связанных с ней позднейших статей является изучение разных теорий относящихся к связи между спектрами истинного (массивного) поглощения и диффузного отражения порошкообразных твёрдых веществ уделяя при этом особое внимание роли и влиянию отдельных параметров (— показатель преломления, — оптическая толщина зерна, — коэффициент отражения). На основе наиболее важных теорий вычислены и подробно проанализированы функции. Анализ даёт ценные информации с точки зрения метрологии — с одной стороны, и указывает на дальнейшее направления экспериментальной работы — с другой стороны.

В статье даётся краткий обзор проблем источников ошибок проявляющихся при измерении и исчерпывающее рассмотрение теории Бодо.