

since both of them have nearly the same greenish blue radiation, but in contrast to other alloys, D-1 as well as D-16 exhibits an increase in intensity at the edge of the plates (a colored border).

The physical meaning of this phenomenon is not completely clear as yet. In every case it was evident that the glowing occurs only with the production of an oxide film and furthermore only with films of a specific structure, for oxide films on aluminum and its alloys, as is known, have a structure different from the films covering other metals like copper, lead, zinc, etc.

This hypothesis is confirmed by the fact that on first switching on the current the glowing does not begin instantaneously, but only after a certain time interval (0.25 to 0.5 sec); then the intensity of the glowing rises to a definite maximum which requires another time interval (2-4 sec). From this observation the glowing seems to accompany a process of formation of an oxide coating of a certain structure. At the conclusion of the formation of the oxide layer the brightness of the glowing remains constant and with subsequent switching of the current the growth described above is not observed. With the removal of the oxide film by boiling the electrode in alkali, the time for growth of the intensity of the glowing increases (4-5 sec), this being the time required for the appearance and growth of the oxide layer. When direct current is passed through a bath having two electrodes made from one and the same alloy it is observed that the glowing occurs only at the anode, i.e., only with motion of the current in the direction: metal, film, solution, and not in the reverse direction. This confirms again the connection between the glowing and the production of an oxide coating, which has control over this same valve action.

By trying a number of electrolytes, it was determined that the brightest glowing occurs in solutions of NaHCO_3 , Na_2HPO_4 , NaH_2PO_4 , Na_3PO_4 , NaOH , KOH . Somewhat weaker glowing occurs in solutions of Na_2CO_3 , $(\text{NH}_4)_2\text{CO}_3$. Still weaker glowing occurs in $(\text{NH}_4)_2\text{SO}_4$, MgSO_4 . The glowing does not occur in acids. The glowing is also absent in solutions of NaCl , KCl , NaBr and KBr . Furthermore, the addition of one of these salts to a solution in which glowing occurs brings about an attenuation and cessation of the glowing, a sharp increase of the voltage in the circuit and a growth of the temperature of the solution toward the boiling point. At the same time, one observes the onset of instantaneous spark discharges and afterwards unstable electric arcs between the electrodes and the solutions⁵.

The concentration of the solutions required for

convenient observation varies in its dependence on the degree of dissociation of a given substance. Thus, for NaHCO_3 , NaH_2PO_4 , 1-2% was sufficient, while for NaOH , KOH a smaller concentration was needed. As the concentration was increased, the intensity of the glowing increased correspondingly, up to a definite limit. With an applied voltage of 220v, upon increasing the concentration of the solution (e.g. NaHCO_3) with the addition of undissolved soda, one can observe a very beautiful phenomenon of instantaneously flashing and extinguishing tiny spark discharges, superficially resembling scintillation. This phenomenon starts up with the introduction of some more soda, but with the passage of time it grows weaker and stops until more soda is added. During the course of these experiments the temperature of the solution experienced an insignificant rise and only with high concentrations and greater current densities did the solution go as far as the boiling point. For moderate concentrations of the solution (e.g., 1-2% NaHCO_3), heating of the electrolyte was almost unobservable (cold glowing) and the temperature of the bath remained constant with the passage of time.

Further studies of this phenomenon will establish its physical meaning and will determine its practical applications; in particular, the ability of each alloy of aluminum to glow with a very specific color may make it possible to bring about the use of the phenomenon for the purpose of spectral-electrolytic analysis.

¹ N. D. Tomashov, *Theory of the Corrosion of Metals*, Metallurgizdat, 1952.

² N. D. Tomashov and A. V. Bialobzheskii, *Research on the Corrosion of Metals*, Tr. In-ta Fiz. Khim. Akad. Nauk SSSR **1**, 1951, p. 136.

³ N. D. Tomashov and M. N. Tiukina, loc. cit. p. 110.

⁴ G. V. Akimov, *Theory and methods of observation of the corrosion of metals*, Acad. Sci. USSR, 1945.

⁵ I. Z. Iasnogorodskii, *Heating of metals and alloys in electrolytes*, Mashgiz (1952).

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The Effect of Absorption of Luminescence on Its Intensity in the Powdered Luminophors

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IN reference 1 the dependence was established of the intensity of luminescence of the powdered

luminophors on the size of the grains, the relative index of refraction, the index of absorption for the exciting radiation, and the thickness of the layer. The absorption of the light of luminescence was not considered. In the present report we considered the influence of the latter factor.

Consider a horizontal infinite slab of thickness x_0 . For the excitation of luminescence, let this slab be uniformly illuminated from above by diffuse monochromatic flux. Because of the heterogeneous nature of the slab, the light is scattered in all directions. Therefore, if we consider a horizontal plane inside the slab, this plane will be illuminated from above and below. Let us call E_1 the illumination from above, and E_2 the illumination from below. Gershun² showed that these illuminations are respectively equal to:

$$E_1(x) = \frac{R^{-1}e^{L(x_0-x)} - Re^{-L(x_0-x)}}{R^{-1}e^{Lx_0} - Re^{-Lx_0}}; \quad (1)$$

$$E_2(x) = \frac{e^{L(x_0-x)} - e^{-L(x_0-x)}}{R^{-1}e^{Lx_0} - Re^{-Lx_0}}$$

$$I_1 = \frac{1}{2} CkB \frac{(1 + R_l) e^{-L_l x_0}}{(1 - R_l^2 e^{-2L_l x_0}) (R^{-1} e^{L x_0} - Re^{-L x_0})} \left\{ \left(\frac{1}{R} + 1 \right) e^{L x_0} \left[\frac{e^{(L_l - L) x_0} - 1}{L_l - L} \right. \right. \\ \left. \left. - R_l \frac{1 - e^{-(L_l + L) x_0}}{L_l + L} \right] - (R + 1) e^{-L x_0} \left[\frac{e^{(L_l + L) x_0} - 1}{L_l + L} - R_l \frac{1 - e^{-(L_l - L) x_0}}{L_l - L} \right] \right\}; \quad (2)$$

and from the side of excitation*:

$$I_2 = \frac{1}{2} CkB \frac{1 + R_l}{(1 - R_l^2 e^{-2L_l x_0}) (R^{-1} e^{L x_0} - Re^{-L x_0})} \left\{ \left(\frac{1}{R} + 1 \right) e^{L x_0} \left[\frac{1 - e^{-(L_l + L) x_0}}{L_l + L} \right. \right. \\ \left. \left. - R_l \frac{e^{-(L_l + L) x_0} - e^{-2L_l x_0}}{L_l - L} \right] + (R + 1) e^{-L x_0} \left[\frac{e^{-(L_l - L) x_0} - 1}{L_l - L} \right. \right. \\ \left. \left. + R_l \frac{e^{-(L_l - L) x_0} - e^{-2L_l x_0}}{L_l + L} \right] \right\} \quad (3)$$

Here L_l and R_l are given in terms of the constant of scattering s_l and the constant of absorption k_l of the light of luminescence. As was shown in reference 1, s and k in many cases can be given in terms of the effective size of the grain d , the index of refraction n , the coefficient of reflection from the surface of the grain r , and the coefficient of packing c :

In case the layer is infinitely thick ($x_0 = \infty$)

Here $L = \sqrt{k^2 + 2ks}$, and $R = 1 + k's - \sqrt{(k/s)^2 + 2k/s}$ is the coefficient of reflection of an infinitely thick layer, s and k are the constants of scattering and absorption, respectively, calculated for unit thickness.

At the expense of the absorption of the scattered light, the object under consideration will luminesce. The spectral density of the light flux radiated above and below by the infinitely thin layer dx from the unit surface will be: $dI = \frac{1}{2} CkB (E_1 + E_2) dx$. Adjacent to this layer on one side is a layer of thickness x , and on the other side — a layer of thickness $x_0 - x$. On these layers the light of luminescence suffers multiple reflections. When we sum all elementary fluxes from the infinitely thin layer and then integrate the resulting expressions over the entire thickness, we find for the intensity of the luminescence from the side opposite to the side of excitation:

$$I_2 = \frac{1}{2} CB (1 - R) (1 + R_l) L_l / (L + L_l). \quad (4)$$

If the light of luminescence is not absorbed by the particles of the luminophors, then $L_l = 0$, $R_l = 1$ and $I_2 = I_0 = CB (1 - R)$, i.e.,

$$I_2 = \frac{1}{2} I_0 (1 + R_l) L_l / (L + L_l). \quad (5)$$

The expression obtained can be used for the conversion of the measured spectrum into the true radiation spectrum.

Let us consider some special cases of Eqs. (2) and (3).

1. The exciting radiation is weakly scattered and is attenuated according to the exponential law. X-rays approximately satisfy this condition. In this case $L = R$; $R \approx 0$ and formulae (2) and (3) are transformed respectively into

$$I_1 = \frac{1}{2} CkB \frac{1 + R_l}{1 - R_l^2 e^{-2L_l x_0}} \left[\frac{e^{-kx_0} - e^{-L_l x_0}}{L_l - k} + R_l \frac{e^{-(2L_l - k)x_0} - e^{-L_l x_0}}{L_l + k} \right], \quad (6)$$

$$I_2 = \frac{1}{2} CkB \frac{1 + R_l}{1 - R_l^2 e^{-2L_l x_0}} \left[\frac{1 - e^{-(L_l + k)x_0}}{L_l + k} - R_l \frac{e^{-(L_l + k)x_0} - e^{-2L_l x_0}}{L_l - k} \right] \quad (7)$$

2. The exciting radiation is weakly scattered and penetrates to a small depth (for instance, α -particles). Therefore, $L = k \gg L_l$; $R \approx 0$ and we obtain:

$$I_1 = \frac{1}{2} CB \frac{(1 - R_l^2) e^{-L_l x_0}}{1 - R_l^2 e^{-2L_l x_0}}, \quad (8)$$

$$I_2 = \frac{1}{2} CB \frac{(1 + R_l)(1 - R_l e^{-2L_l x_0})}{1 - R_l^2 e^{-2L_l x_0}}.$$

When $x_0 = \infty$

$$I_2 = \frac{1}{2} CB(1 + R_l), \quad (9)$$

i.e., with the increase of the size of the grain (d), the coefficient of reflection R_l decreases and, consequently, I_2 decreases.

3. The exciting radiation is weakly scattered and weakly absorbed (gamma rays). In this case the layer is found to be uniformly excited for sufficiently great thicknesses, and, therefore,

$$I_1 = I_2 = \frac{CkB}{2L_l} \frac{1 + R_l}{1 - R_l^2 e^{-2L_l x_0}} [1 - e^{-2L_l x_0} + R_l (e^{-2L_l x_0} - e^{-L_l x_0})].$$

For an infinitely thick layer, $I_1 = 0$ and $I_2 = \frac{1}{2} CkB \times (1 - R_l)^{1/k_l}$, i.e., with the increase of d , the coefficient of reflection decreases and I_2 increases.

In such a way the different nature of the attenuation of the excitation flux leads to the result that an increase of the crushing of the powder of the luminophor increases the brightness of the luminescence in one case and decreases it in the second. Therefore we can imagine a case in which the brightness of the luminescence depends weakly on the degree of dispersion.

* The formulas obtained are indeterminate if the light of the luminescence is not absorbed. In this case it is necessary during the calculation to use the formulas

$$t(x) = 1/(1 + s_l x) \quad \text{and} \quad r(x) = s_l x/(1 + s_l x) \quad (\text{see}$$

reference 3). As a result, expressions are obtained which coincide with the formulas for the intensity of luminescence, given in reference 1.

¹ A. P. Ivanov, J. Exper. Theoret. Phys. USSR 26, 275, (1954).

² A. A. Gershun, Trudy GOI 11, 99, 43 (1936).

³ M. M. Gurevich, Trudy GOI 6, 57, 1, (1931)

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Concerning Some Thermodynamic Inequalities

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IN the thermodynamic investigation of the properties of materials which possess magnetic and dielectric properties that obey the general law set forth, for example, in reference 1, it is possible to obtain thermodynamic inequalities which are the necessary conditions for thermodynamic equilibrium. The present communication is devoted to a brief derivation of such inequalities, and to the obtaining, with the help of the latter, of certain conclusions as to the form of the equilibrium curve of the magnetization of a magnet.

Assuming that each element of the volume of a body is in a state of thermodynamic equilibrium, we can represent the first law of thermodynamics, for media of interest to us, in the following form

$$\Delta e = T\Delta s + (H\Delta B + E\Delta D)/4\pi. \quad (1.1)$$