LXXXII.—*The Budde Effect in Bromine. Part II. The Kinetics of the Reaction and the Light Absorption of Wet and of Dry Bromine.*

By BERNARD LEWIS and ERIC KEIGHTLEY RIDEAL.

IN Part I evidence was presented for the view that the photoactive constituent responsible for the Budde effect in moist bromine is a bromine hydrate of composition Br_2,H_2O which is present both in the homogeneous gas phase and on the walls of the containing vessel. The adsorption isotherm equation was shown to be applicable to the partition of the hydrate between the two phases.

It was considered of interest to examine the properties of this bromine hydrate in more detail.

The Equilibrium Constant and Heat of Formation.

From a determination of the Budde effect at various temperatures the alteration of the equilibrium

$$Br_2 + H_2O \rightleftharpoons Br_2,H_2O$$

can be determined. The determinations were carried out with the apparatus described in the previous communication. A low partial pressure of water was employed so that the Budde effect was due almost entirely to the adsorbed bromine hydrate. The following values were obtained, t being the temperature of the bath, and K/K_p the deflection in scale divisions :

t	99°	81°	63°	41°	22°
K/K_p	86	95	106	122	140

The deflection decreases, or the equilibrium constant, K_p, where

$$K_p = [Br_2][H_2O]/[Br_2,H_2O],$$

increases, with elevation of the temperature.

Since an intense light was employed and the bromine hydrate concentration was low, the deflection is proportional to the concentration of the hydrate on the surface and may be employed in the van t Hoff isochore to calculate the heat of formation.

Inserting the above values in the equation

$$2{\cdot}3 \log_{10} \frac{K_1}{K_2} = \frac{Q}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

we obtain the following values (in calories) for Q : $Q_{81^\circ} = 1440$, $Q_{63^\circ} = 1425$, $Q_{41^\circ} = 1340$, $Q_{22^\circ} = 1336$.

Since $Q_t = Q_0 + \beta T^2$, where $2\beta =$ the difference in specific heat of reactants and products, we obtain

$$\beta = 0{\cdot}0028 \text{ and } Q_0 = 1090 \text{ cals.}$$

Thus the heat change in the formation of the hydrate in the surface phase can be expressed as follows :

$$Br_2 + H_2O = Br_2,H_2O + 1090 \text{ calories.}$$

The magnitude of Q_0 is in agreement with expectations regarding the heat of formation of such an unstable compound; it is practically identical with the heat change on solution of bromine in water :

$$Br_2 \text{ (liq)} + H_2O \text{ (600 mols.)} \longrightarrow Br_2 \text{ aq} + 1080 \text{ calories.}$$

From a knowledge of the heat of reaction it is possible, with the aid of the approximation equation of the Nernst heat theorem, to calculate the value of the equilibrium constant.

Inserting the values $Q_0 = 1090$ (if there is a difference in the heat of formation in the surface phase and the bulk phase it cannot be very large, for the heat of formation is already so small. We may therefore without serious error assume 1090 cal. as the heat of formation in the bulk phase), $T = 313°$ K, $\Sigma\nu = 1$, and $\Sigma\nu C = 3$ in the equation

$$\log_{10} K_p = \frac{-Q_0}{4{\cdot}571T} + 1{\cdot}75\, \Sigma\nu \log T + \Sigma\nu C,$$

we obtain $\log_{10} K_p = 6{\cdot}61$ or $K_p = 4{\cdot}10 \times 10^6$ in atmospheres $= 3{\cdot}10 \times 10^9$ in mm.

From this value we find that with a partial pressure of bromine of 200 mm. and of water vapour of 10 mm. the partial pressure of the hydrate will be $0{\cdot}65 \times 10^{-6}$ mm., equivalent to a concentration of $3{\cdot}86 \times 10^{-11}$ g.-mol. per litre in the bulk phase.

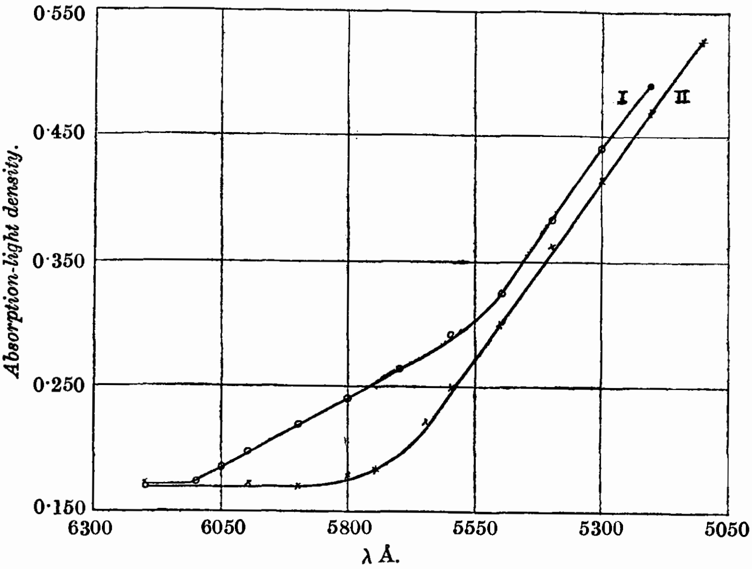
The increase of pressure on illumination has been taken as a measure of the equilibrium constant at various temperatures. Such a procedure is justified, since the Budde effect has already been shown to be proportional to the concentration of the hydrate and the large value of K_p for the equilibrium constant indicates that the equilibrium concentration of the hydrate is always so small that even large alterations in its concentration due to alteration in the temperature cannot affect the concentration of bromine or water, which may be regarded as constant.

The Absorption Spectrum.

If this small quantity of bromine hydrate is the photoactive constituent, it must possess properties different from those of dry bromine. An examination of the absorption spectra of wet and of dry bromine revealed interesting differences.

In Fig. 1 are plotted the absorption curves for wet and for dry bromine determined with the aid of a Nutting spectrophotometer (zero = 0·173), the dry bromine being retained in a clear quartz polarimeter tube which, previously to the admission of bromine, stored over phosphoric oxide for 9 to 10 months, had been thoroughly ignited whilst a high vacuum was maintained in the system.

FIG. 1.



I. *Wet bromine.* II. *Dry bromine.*

The curves indicate that whilst ordinary bromine in wet vessels commences to show a definite absorption at λ = 6100 Å., the dry bromine shows no marked absorption before λ = 5700 Å. If light absorption is taken as a criterion of molecular excitation, the complex bromine–water requires an energy of excitation 3200 calories per g.-mol. less than that of dry bromine (2·05 volts compared with 2·20 volts) and it might be suggested that the catalytic effect of water vapour in many reactions may in part be due to the lower critical energy increment required for excitation of the complex hydrate.

Whilst the absorption of radiation by the hydrate results in the degradation of the radiant energy, dry bromine absorbs radiation of light of $\lambda = 5700$ Å. This light, however, does not reappear as thermal energy, for dry bromine shows no Budde effect. It must be concluded that such light which does not pass through the tube and is not degraded to heat must be either reflected or absorbed and re-emitted by the dry bromine molecules in the direction of the sides of the tube, *i.e.*, must be emitted as resonance radiation or fluorescence. In the presence of water vapour more light is absorbed and fluorescence would be reduced. The possible extinction of such fluorescence in dry bromine by water vapour would appear to have its counterpart in the extinction of fluorescent mercury by gases such as hydrogen and water vapour noted by Stuart (*Z. Physik*, 1925, **32**, 262) and the extinction of fluorescence by water vapour in hydrogen and oxygen mixtures noted by Baker. It would further suggest the emission and absorption of light from molecule to molecule in a dry gas until absorption by a hydrate molecule occurred as a mechanism for chain reactions. Several experiments were devised to detect the difference between the nature of the light emitted from the sides of narrow tubes containing wet and dry bromine respectively, down the axes of which narrow pencils of yellow light were passed. Whilst no quantitative data could be obtained, the light emitted from the dry bromine appeared somewhat yellower, *i.e.*, richer in the rays absorbed by bromine, than the reddish light from the wet tube.

The Stark–Einstein Law of Photoequivalence.

An attempt was made to establish the validity of the Stark–Einstein law of photochemical equivalence in the case of the Budde effect. The measurements of the absorption of energy by the reaction vessel containing bromine were made with a black-body radiation meter. The meter consisted of a flat black receiving bulb with compensator and aniline gauge and was calibrated by the method of internal electric heating with the aid of a small platinum spiral in the interior; the whole system being carefully lagged and preserved from any slight air currents which might affect either the steadiness or accuracy of reading. Due corrections were made for the resistance of the circuit and leading-in wires. The following calibration values were obtained:

Room temperature 20·2°. Reading in scale div.	Cal./sec.	Ergs per sec. per 10 div. × 10^{-4}.
3·5	$5\cdot36 \times 10^{-4}$	6·42
4·7	$7\cdot73 \times 10^{-4}$	6·88
6·8	$1\cdot29 \times 10^{-3}$	7·93
10·7	$2\cdot55 \times 10^{-3}$	10

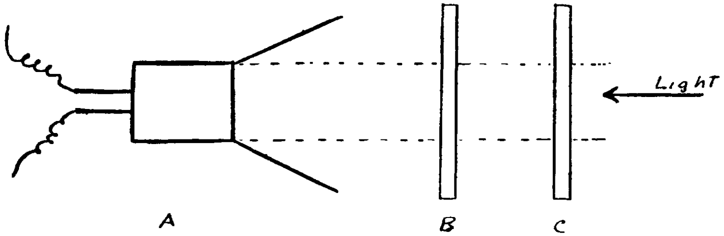
In a typical experiment with light between 5300—5700 Å. it was found that the bromine absorbed energy, as measured by the radiation meter, of $1{\cdot}53 \times 10^4$ ergs per second, yielding a Budde effect of 184·8 bars.

As has already been indicated, part of the light apparently absorbed by the bromine, *i.e.*, not transmitted to the radiation meter, is emitted from the sides of the tube in the form of fluorescence. It was necessary to find out how much of the energy of $1{\cdot}53 \times 10^4$ ergs per second was emitted as fluorescence, *i.e.*, apparently absorbed by dry bromine, and how much contributed to the Budde effect by absorption by the bromine hydrate. The following arrangement (Fig. 2) was accordingly devised to evaluate this fraction :

A. Moll thermopile.

B. A reaction vessel similar to C containing moist bromine at the same partial pressure, or air.

FIG. 2.



C. Reaction vessel containing either dry bromine in contact with phosphoric oxide, or air.

The two reaction vessels were of similar size and shape, both with plane and parallel sides immersed in a trough through which water from a thermostat was circulated. The point light lamp, water trough, collimator, and screens were used as heretofore. After the lamp had been so adjusted that a constant deflection was obtained on the Moll thermopile with the bulbs containing dry air, dry bromine was first admitted to bulb C at a partial pressure of 120 mm. The deflection on the thermopile was noted and moist bromine (saturated at 17°) admitted to B until the partial pressures of the bromine in the two bulbs were identical. The deflection was again noted and the bromine in the bulb C was replaced by dry air; the final determination of the radiation transmitted to the thermopile was then made. These operations were repeated, reversing the procedure in each case, and the following average readings were obtained :

$\left.\begin{array}{l}\text{B containing air}\\ \text{C containing dry bromine}\end{array}\right\}24{\cdot}80$ $\quad\left.\begin{array}{l}\text{B containing dry air}\\ \text{C containing dry air}\end{array}\right\}25{\cdot}43$

$\left.\begin{array}{l}\text{B containing moist bromine}\\ \text{C containing dry air}\end{array}\right\}23{\cdot}97.$

These results indicate that the apparent absorption by dry bromine is represented by 0·63 division on the Moll thermopile, that by wet bromine by 1·46 divisions; or about 43·2% of the light apparently absorbed by the moist bromine is emitted again in the form of radiation, as it does not contribute to the thermal energy to which the Budde effect is due.

The areas under the absorption curves between wave-lengths 5400 Å. and 6100 Å. will give the percentage absorptions due to wet and to dry bromine (wet bromine absorbs up to 6100 Å.; the filter transmitted the red rays):

Area under dry curve = 3130. Area under wet curve = 6530.
% absorbed by dry Br_2 = 48. % absorbed by wet Br_2 = 52.

All the light absorbed by the unhydrated bromine in the wet bromine is not emitted as fluorescence from the sides of the vessel. A part of it is reabsorbed by the hydrated molecules and degraded into heat energy. What proportion is reabsorbed we have no means of determining from our data. It must be borne in mind that as far as the absorption spectra curves are concerned it makes no difference how much of the emitted light is reabsorbed, since only a small portion of this light, even if not reabsorbed, would find its way through the spectrophotometer.

Accordingly, of the $1{\cdot}63 \times 10^{4}$ ergs per second apparently absorbed, or not transmitted by the wet bromine, in the previous experiment, 56·8% is actually absorbed and 43·2% emitted as radiation, or $0{\cdot}926 \times 10^{4}$ ergs per second are absorbed. The mean wave-length of light employed was 5550 Å., for the energy distribution curve of the radiation passing through the filter was flat within the region 5300 Å.—5800 Å. or the mean quantum was $3{\cdot}53 \times 10^{-12}$ erg; the number of quanta actually absorbed by the bromine hydrate per second is accordingly $0{\cdot}926 \times 10^{4}/3{\cdot}53 \times 10^{-12}$ or $2{\cdot}62 \times 10^{15}$ quanta per second.

The Budde effect was 184·8 bars, corresponding to a heat evolution, as determined from the curve given in Part I, of $1{\cdot}26 \times 10^{4}$ ergs per second. If this heat is evolved by the conversion of quanta of magnitude $3{\cdot}53 \times 10^{-12}$ erg into kinetic energy in the decomposition or deactivation of the excited bromine hydrate molecules, we obtain as the number of molecules undergoing such a process of deactivation or decomposition per second $1{\cdot}26 \times 10^{4}/3{\cdot}53 \times 10^{-12}$ or $3{\cdot}57 \times 10^{15}$.

In the following table are the results of three different experiments performed in the above manner. Figures in the third column are obtained by multiplying the calibration value in the previous table by 1·11 to allow for diffusive reflection of lampblack.

Exp.	Temp.	Mano-meter diff.	Total ergs per sec. not trans-mitted $\times 10^{-4}$.	Quanta per sec. absorbed by the hydrate $\times 10^{-15}$.	Budde effect in bars.	Ergs per sec. equiv-alent $\times 10^{-4}$.	Mols. per sec. decom-posing $\times 10^{-15}$.	Mols. per quanta.
2	20·8°	2·28	1·63	2·62	184·8	1·26	3·57	1·36
3	20·9	2·43	1·73	2·78	186	1·30	3·68	1·32
4	20·2	1·73	1·24	2·00	149	1·01	2·82	1·41

These calculations were made under extreme conditions allowing for no absorption by the hydrate molecules of the re-emitted radiation from dry bromine. Taking this into account would bring the figures in the last column close to unity.

However, it will be noted from the data in the last column that the agreement between the number of quanta absorbed per second by the hydrate and the number of such molecules decomposing per second with the liberation of the energy of activation in the kinetic form is sufficiently close to show the validity of the Stark–Einstein law of photoequivalence in the case of the Budde reaction.

The Absorption Coefficient of the Hydrate.

On the hypothesis that the photoactive constituent is a bromine hydrate it is possible from a consideration of its concentration and the magnitude of the Budde effect, which is a measure of the light actually absorbed by the hydrate, to effect a determination of the absorption coefficient. The actual bulk concentration of hydrate for definite partial pressures of bromine and water can be determined only on the assumption that the concentration equilibrium of the reaction

$$Br_2 + H_2O \rightleftharpoons Br_2,H_2O$$

is not sensibly affected whether the water vapour and the hydrate are in the surface or bulk phases, an assumption which is only valid if the activity coefficients of the reactants do not change sensibly during adsorption, or that the change in the activity coefficient of the water on adsorption is the same as the change effected in this function of the bromine hydrate. Since the heat of formation of bromine hydrate is small, some measure of support is given to the latter hypothesis. We will therefore employ the value for K_p determined above as $3·10 \times 10^9$ when expressed in mm. of mercury.

From the curves given in Fig. 2 (Part I of this investigation), in which the increase in Budde effect with increasing water-vapour pressure at a constant bromine pressure is plotted, it is seen that at a pressure of 0·0415 mm. of water and a pressure of 158 mm.

of bromine, a Budde effect of 115 bars was caused by the bromine hydrate in the gas phase, out of a total of 2140 bars (maximum deflection under the intensity of illumination employed).

Thus 5·4% of the light was absorbed by the bromine hydrate present in the gas phase, which was 2·35 cm. deep, or 94·6% would have been transmitted if no surface phase existed. The partial pressure of the hydrate in the gas phase can with the proviso indicated above be determined with the aid of the equilibrium constant or

$$[Br_2][H_2O]/[\text{Hydrate}] = 3{\cdot}10 \times 10^9 = 158 \times 0{\cdot}0415/[\text{Hydrate}],$$

whence the partial pressure of the hydrate is $2{\cdot}1 \times 10^{-9}$ mm. From Beer's law, $I_t = I_0e^{-kcd}$, where I_0 is the entering light, I_t the transmitted light, c the concentration, d the thickness, and k the absorption coefficient of the hydrate, we obtain :

$$\log_e (I_t/I_0) = -\, kcd,$$

or $$2{\cdot}3 \log_{10} 0{\cdot}946 = -\, kcd = -\, k(2{\cdot}1 \times 10^{-9}) \times 2{\cdot}35,$$

whence $$k = 10{\cdot}7 \times 10^6.$$

In a similar manner, for a point where $P_{H_2O} = 0{\cdot}083$ mm. we find a Budde effect, in the gas phase, of 230 bars or 10·75% light absorption, whence $I_t/I_0 = 0{\cdot}8925$ and $k = 11{\cdot}4 \times 10^6$. For the low partial pressure of $P_{H_2O} = 0{\cdot}02$ mm. we find a Budde effect in the gas phase of 55 bars, equivalent to 2·57% light absorption or 97·43% light transmitted, whence $k = 9{\cdot}6 \times 10^6$. The mean value of the absorption coefficient is thus $10{\cdot}5 \times 10^6$.

It is interesting to compare this value with that obtained by Wood (*Physikal. Z.*, 1912, **13**, 353) for the absorption of the light ($\lambda = 2537$ Å.) by mercury vapour. He found that the intensity of this light was reduced by one-half by passage through a layer of mercury vapour 5 mm. thick and at a partial pressure of 10^{-4} mm. Inserting these values in the equation, we obtain

$$2{\cdot}3 \log_{10} 0{\cdot}50 = -\, k \times 10^{-4} \times 0{\cdot}5, \text{ whence } k = 0{\cdot}14 \times 10^6.$$

Thus the absorption coefficient of bromine hydrate in the spectral region which produces excitation is comparable in value with that of mercury vapour for its resonance line. On the hypothesis of Ornstein that the range of influence of a quantum of light is proportional to the square of the wave-length, the absorption coefficient of bromine hydrate for light of $\lambda = 5550$ Å. should be some four times that of mercury vapour.

Mechanism of the Budde Effect.

The first elementary process in a photochemical action is, as Stern and Volmer (*Z. Wiss. Photographie*, 1920, **19**, 275) were the first to show, not the primary reaction but the excitation of the molecule by absorption of radiation. On the hypothesis that there exist in moist bromine both bromine and bromine hydrate molecules, the primary processes of light absorption are the conversion of these into active molecules :

$$Br_2 + h\nu \longrightarrow Br_2'. \quad Br_2,H_2O + h\nu \longrightarrow Br_2',H_2O.$$

We have seen that in the case of dry bromine no Budde expansion occurs, although light absorption undoubtedly takes place. The excited bromine molecules must thus lose their energy of excitation in the form of radiation. Whether the radiation emitted from an excited bromine molecule in the interior of the gas passes through the gas to the outer walls or undergoes a series of absorptions and emissions from numerous molecules in the operation of transfer of a quantum from the interior to the surface, or, again, whether the energy of the excited molecule is handed on by collision within the life of the excited molecule, *viz.*, 10^{-7} second, thus forming a chain, cannot be established with certainty. As in the case of the resonance line of mercury vapour, if the light is emitted from the bromine molecules as light of the same wave-length as the absorbed light, the course of the fluorescent light is interrupted in its path to the surface by its absorption by hydrate molecules, thus materially reducing the strength of the fluorescent light.

We have seen that only when a bromine molecule is moist, *viz.*, a bromine hydrate, do we obtain a Budde effect or conversion of the light energy into thermal energy. The frequency, ν, of any line may be considered as the sum $\nu = \nu^e + \nu^n + \nu^m$, where e is the electronic, n the oscillatory, and m the rotational quantum number (Mulliken, *Physical Review*, 1925). In absorbing a quantum, not only may the quantum level of the electron be changed, but also the oscillatory and rotational quantum energy levels. In the case of iodine at low pressures (Oldenberg, *Z. Physik*, 1923, **18**, 1), the molecule, without dissociating, can absorb and re-emit as a resonance spectrum an amount of energy five times the work of dissociation when it is illuminated by light of wave-length $\lambda = 1849$ Å. The explanation advanced is that the excitation energy is primarily employed in raising the electron system to a higher quantum state, whilst the oscillation and rotation energies are only altered by the coupling of their periods with those of the electron system. But we may have, in the case of the halogens, marked changes in the oscillation energy where the absorption of light alters the potential energy of the nuclei, thus altering the strength of chemical binding of the molecule. In the excited electronic state, the energy required for dissociation is less than in the normal state, and if the alteration in the oscillation quanta is sufficient to cause the potential energy of the nuclei to become greater than the dissociation energy for the excited state the molecule will fly apart. There is indeed a correlation between a large change in oscillation quantum number and a considerable alteration of the strength of binding on excitation. As a measure of the strength of binding we can utilise, for qualitative estimates, the direction of the shading of the bands, which is an indication of change in the moment of inertia of the molecule. The band spectra of iodine investigated by Mecke (*Ann. Physik*, 1924, **71**, 104) show a convergence limit of the oscillation quantum states at 5000 Å. Wave-lengths, therefore, of 5000 Å. or less will dissociate iodine under certain conditions. The convergence limit for bromine has been placed by Franck (see Part I, *loc. cit.*) at about the same wave-length from the position of the long wave-length limits of the continuous spectra which are known.

The light used in this investigation being of considerably greater wave-length, dry bromine would not be expected to dissociate. That dissociation does not occur is proved further by the work of Ludlam (see Part I, *loc. cit.*), who found no Budde effect with dry bromine illuminated with ultra-violet light containing energy many times that necessary for dissociation.

It would appear that in the case of bromine hydrate the lowering of the critical energy increment for dissociation into atoms is very great. Dissociation may occur thus :

(1) $Br_2,H_2O + 51{,}500$ calories $= 2Br + H_2O + 4410$ calories,

where 51,500 calories is the energy of the radiation of wave-length employed in these experiments, some 4410 calories greater than the threshold value, as is confirmed by the commencement of absorption at 6100 Å. The recombination of the bromine and water to re-establish equilibrium gives rise also to the evolution of the heats of combination :

(2) $2Br = Br_2 + 46{,}000$ calories.
(3) $Br_2 + H_2O = Br_2,H_2O + 1090$ calories.

The same type of mechanism is given by the calculations of Christiansen (*Dansk Vid. Math. Phys. Medd.*, 1919, **1**, 14) for the reactions

$Br + HBr + 43{,}700$ calories $= Br_2 + H + 12{,}400$ calories
and $HBr + 112{,}000$ calories $= H + Br + 35{,}000$ calories.

Thus 47,090 calories appears to be close to the critical energy that must be absorbed by bromine hydrate before any Budde effect can be expected. The absorption of light of greater frequencies, for a given constant quanta absorption, merely increases the heat effect on the right-hand side of the equation (1) and thus the Budde effect.

Summary.

The heat of formation of bromine hydrate is 1090 calories, comparable with the heat of solution of liquid bromine in water, whilst the equilibrium constant for the dissociation of bromine hydrate at 313° K is of the order of $3{\cdot}10 \times 10^9$. The absorption curves of wet and of dry bromine have been compared; marked absorption commences at $\lambda = 6100$ Å. for the wet and at $\lambda = 5700$ Å. for the dry gas; this corresponds to a lowering of the critical energy increment of excitation of 3200 calories. When corrected for the absorption and probable fluorescence of dry bromine, it is found that the Stark–Einstein law of photoequivalence is obeyed, a maximum of 1·41 molecules per quantum being obtained. The absorption coefficient of bromine hydrate for the spectral region employed is $10{\cdot}5 \times 10^6$, comparable with that obtained by Wood, $0{\cdot}14 \times 10^6$, for mercury vapour for the line $\lambda = 2537$ Å. A mechanism of excitation and decomposition of bromine hydrate molecules is advanced in explanation of the Budde effect.

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THE LABORATORY OF PHYSICAL CHEMISTRY,
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