ACTIVATION ENERGY OF DECOMPOSITION REACTIONS OF SOLIDS

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On studying the kinetics of the thermal decomposition of ferrous sulphate, sodium disulphite, and potassium hydrocarbonate, it was found that the relation among the activation energy, rate constant, and temperature can be solved on the basis of the Planck radiation law applied to the internal planes of a crystal.

There are two fundamental approaches to the kinetics of the decomposition of solids, the geometric and the molecular-kinetic one. For the correlation of the plots η (the fraction decomposed) *vs* time mathematical treatments are used, which are based on several known equations established[1] for the rate of the phase boundary advance, for nucleation, growth and branching of nuclei of the solid product; these are the main features of the geometric approach. The molecular-kinetic treatment of kinetic data is based on modifications of the Polanyi–Wigner equation[1], *e.g.*

$$-\mathrm{d}n/\mathrm{d}t = s v_{\mathrm{f}} \bar{n} S \exp(-E/RT) = k_1 S. \qquad (I)$$

The frequency factor v_{f} should have a value $\approx 5 . 10^{12}$ s^{-1}; in some cases much higher values appear, *viz.* as much as 10^{34} s^{-1}. The decomposition reactions of solids are complicated and the calculated activation energy in some cases may not be in accordance with the actual energy quanta involved in the activation[2]. According to Garner[1], Eq. (*I*) holds only in case that the decomposition takes place reversibly and the activation energy is equal to the reaction enthalpy of the decomposition reaction. In case of the irreversible reaction, the activation energy is greater than the reaction enthalpy and the Polanyi–Wigner equation is not suitable for the description of the kinetics of decomposition.

For the reactions of the type A (s) → B(s) + C (g), the escape of gaseous product must be enabled in order that the reaction may take place. In case of a compact single crystal, this transfer of matter seems to be enabled only from the surface of so far unreacted part of the crystal. The displacement of boundary to the inside of crystal during its decomposition is considered sometimes the process controlling the kinetics of decomposition of even small crystals where a direct observation is difficult and where this mechanism is judged on the basis of mathematic treatment of experimental data. The displacement of boundary can be observed as well during the decomposition of porous polycrystalline object and the condition of the boundary occurrence is not therefore the compactness of the decomposed solid object. Hills[3] established that the decomposition of tablets of compressed limestome crystals takes place on a sharp boundary between the undecomposed limestone and the outside layer of porous lime and that the decomposition is kinetically controlled by the heat transfer to this boundary and by the transfer of CO_2 out of the boundary and not by the chemical reaction. At the beginning of heating big ($\sim$ cm) solid objects, a temperature gradient results from limited thermal conductivity, the surface has a higher tem-

perature than the inside of crystal and from this reason, above all, the decomposition must proceed from the surface to the interior of the crystal.

To explain the course of the decomposition process in a crystal, every model requires consequently a heat energy supply and it must solve the problem of the source and transfer of this energy. In case of a solid substance, the transfer is enabled in the main by conduction, to the surface as well by radiation. However, at a low rate of decomposition reaction it is possible, in case of a small body, to attain practically identical temperature over whole its section and for the irreversible decomposition reactions, neither the heat transfer, nor the mass transfer will be then the controlling process. As the crystals of the decomposition solid product formed on the surface of the decomposing crystal have a size of order up to 10^{-5} m (ref.[4]), the phase boundary must be diffusive and it is possible to imagine that with small crystals of the micron sizes the decomposition may take place simultaneously in whole volume of crystal. The decomposition will be then controlled by the chemical process and for such a case it is possible to solve the problem of origin of the energy activating the decomposition reaction in a crystal. For this study, fine crystalline substances with a sufficiently high activation energy of decomposition will be suitable in order that the mass transfer effect may be suppressed. At the beginning of the decomposition reaction in crystal A, every energy quantum, sufficient for the activation of the reaction will react according to the equation $A + h\nu \rightarrow A^*$, where A^* denotes an activated state. This process has to be of the elementary process character which will be meant as a complex of changes of the same kind in crystal which are provoked only by certain quanta of energy according to the relation

$$N_A h\nu \gtrless \Delta E^* . \tag{2}$$

Supposing that the controlling process is irreversible and that at a number $M > M_1$ of structural units capable of reacting per unit area of the crystal plane every energy quantum satisfying the relation (2) will react at the beginning of the reaction, it will be possible to consider the reaction in the beginning as the zero-order reaction:

$$k_0 = \lim_{t \to 0} d\eta/dt = Y/M . \tag{3}$$

Let us assume that local energy fluctuations originate in all, even in inside planes of crystal with the largest number of structural units in accordance with the Planck radiation law for an ideal black body. By using the Planck law, we obtain for $\nu_1 > 10^{14}$ s^{-1} and $T < 2000$ K the relation

$$U = \left(4\pi k T \nu_1^3/c^2\right) \exp\left(-h\nu_1/kT\right) . \tag{4}$$

The number of energy fluctuations fulfilling Eq. (2) is given by the relation

$$Y = U/h\nu_{mean} , \qquad (5)$$

where ν_{mean} is defined by the relation

$$\int_{\nu_1}^{\infty} \frac{\nu^3 \, d\nu}{\exp(h\nu/kT) - 1} = 2 \int_{\nu_{mean}}^{\infty} \frac{\nu^3 \, d\nu}{\exp(h\nu/kT) - 1} . \qquad (6)$$

For $\nu_1 > 10^{14} \text{ s}^{-1}$ we can put $\nu_{mean} = \nu_1$ because e.g. for $\nu_1 = 4 . 10^{14} \text{ s}^{-1}$ at 880 K $\nu_{mean} = 4.15 . 10^{14} \text{ s}^{-1}$, thus

$$Y = (4\pi k T \nu_1^2/hc^2) \exp(-h\nu_1/kT) . \qquad (7)$$

By combining Eqs (3) and (7), the relation is obtained

$$k_0 = (4\pi k T \nu_1^2/Mhc^2) \exp(-h\nu_1/kT) . \qquad (8)$$

The Arrhenius relation requires further the validity of

$$-d\ln k_0/d(1/T) = T + h\nu_1/k = E/R . \qquad (9)$$

Then the relation holds

$$E = RT + N_A h\nu_1 . \qquad (10)$$

Eq. (10) corresponds to the relation between the Arrhenius activation energy and the activation internal energy according to the theory of transition states[5], $E = RT + \Delta E^{\ddagger}$, so that $\Delta E^{\ddagger} = N_A h\nu_1$, which is in agreement with the definition relation (2). The frequency factor A of the Arrhenius equation for a decomposition reaction of solid substance is then given by the relation:

$$A = (4\pi e k^3 T/Mh^3 c^2)(E/R - T)^2 , \qquad (11)$$

so that

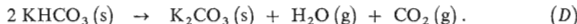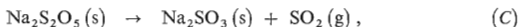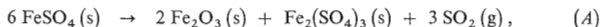$$k_0 = (4\pi e k^3 T/Mh^3 c^2)(E/R - T)^2 \exp(-E/RT) , \qquad (12)$$

$$\log k_0 = 15.536 + \log T + 2\log(E/R - T) - E/2.303RT - \log M . \qquad (13)$$

The frequency factor A is a function of E and T, however, $\log k_0$ in Eq. (13) is linearly dependent on $1/T$ for $T < 2000$ K. From Eq. (11) theoretical values of A were

calculated for $E = 10-70$ kcal/mol and for temperatures at which, according to the relation (13), log $k_0 = -3$ for those activation energies (since this value is usually in the interval of values k_0 measured experimentally). The dependence of A on E is represented in Fig. 1. For M it was inserted $5 \cdot 10^{18}$ m^{-2}; reasons for this value will be given later. In the same figure a dependence is represented which was constructed from the theoretical values of A determined in terms of the graphical extrapolation of straight lines (13) to the value $1/T = 0$. The difference between both dependences is not substantial.

The value of number M is determined approximately from the distance between the nearest structural units, most simply from ionic radii or from density and molecular weight.

Another aim of this work is to verify the hypothesis suggested in terms of the study of kinetics of decomposition of some solid substances:

$$6\,FeSO_4\,(s) \;\rightarrow\; 2\,Fe_2O_3\,(s) \;+\; Fe_2(SO_4)_3\,(s) \;+\; 3\,SO_2\,(g)\,, \qquad (A)$$

$$CaCO_3\,(s) \;\rightarrow\; CaO\,(s) \;+\; CO_2\,(g)\,, \qquad (B)$$

$$Na_2S_2O_5\,(s) \;\rightarrow\; Na_2SO_3\,(s) \;+\; SO_2\,(g)\,, \qquad (C)$$

$$2\,KHCO_3\,(s) \;\rightarrow\; K_2CO_3\,(s) \;+\; H_2O\,(g) \;+\; CO_2\,(g)\,. \qquad (D)$$

EXPERIMENTAL

Redox Disproportionation of Ferrous Sulphate

The sample of ferrous sulphate No 1 was prepared by dehydrating $FeSO_4.7\,H_2O$ (pure reagent, Lachema) by heating to 350°C under nitrogen protective atmosphere. The sample contained 97·2% $FeSO_4$ and 2·1% $Fe_2(SO_4)_3$. According to the X-ray structural analysis this sample corresponded to anhydrous $FeSO_4$. The sample No 2: 140 g $FeSO_4.7\,H_2O$ was dissolved in 200 ml water, moderately acidified with H_2SO_4, heated up and filtered over. To the filtrate, 100 ml of ethanol was added after cooling and crystals of $FeSO_4.7\,H_2O$ were excluded while cooling and stirring which were, according to the X-ray structural analysis, a pure heptahydrate. After washing with ethanol and ether, the crystals were dried in a desiccator by alternating vacuum and nitrogen atmosphere. A 10 g of this specimen was heated for 15 min at 180°C in a stream of nitrogen. The obtained sample No 2 had the composition: 88·6% $FeSO_4$, 0·18% $Fe_2(SO_4)_3$. As to the structure it corresponded to pure $FeSO_4.H_2O$.

Since ferrous sulphate recrystallizes to a transition structure[6] before disproportionation and just this form reacts according to Eq. (A), the size of crystals of the transition structure and not of crystals of initial hydrate or of anhydrous $FeSO_4$ is significant for the mechanism of decomposition. We can judge of the size of crystals of the $FeSO_4$ transition structure from the results of measurements of specific surface area which corresponds to 0·6 μm on the assumption of monodispersity of sample.

A 5 g porcelain boat with a 75 or 150 mg sample was inserted into a quartz tube 17 mm in diameter, placed horizontally in a resistance furnace and purged with nitrogen in advance, up to the junction of Pt/PtRh thermocouple which was introduced into the tube from the opposite side. Gaseous reaction products were carried along with a stream of nitrogen (of purity for filling lamps) at 150 or 300 ml/min which was washed beforehand by a solution of sodium dithionite and hydroxide to remove trace amounts of oxygen, then by concentrated H_2SO_4 and finally by solid KOH. Sulphur dioxide was absorbed in a solution of starch and continuously titrated with $0.1 \text{N-}I_2$.

Decomposition of Calcium Carbonate

Precipitated $CaCO_3$ (ČsI-2, Lachema) was used. Its prevailing size of crystals was 5 μm. The decomposition was carried out in the same furnace and on the same boat as in case of the $FeSO_4$ decomposition. Carbon dioxide resulting from decomposition was carried away with nitrogen at a flow rate of 250 ml/min and trapped in a weighed system consisting of a "Kali" absorption apparatus with KOH solution and a U-tube with molecular sieve Potasit 3.

Decomposition of Sodium Disulphite

Sodium disulphite, a pure reagent (Lachema) was used. Crystals with surface dimensions $0.1 \times \times 0.2$ mm prevailed. The decomposition was carried out in an electric furnace consisting of an outside heated aluminium cylindric block with holes for a regulating thermometer and for a glass tube 18 mm in diameter into which the sample on boat was inserted. Temperature in the tube was measured by a mercury thermometer. It was used partly the 5 g porcelain boat, partly a glass boat made of a microscope cover glass weighing 0.1 g. The height of the sample layer was approximately the same in both cases. Sulphur dioxide formed in decomposition was carried away either by nitrogen or by dry air at a rate of 150 ml/min and in the course of absorption determined by titrating with $0.1 \text{N-}I_2$.

Decomposition of Potassium Hydrocarbonate

$KHCO_3$, an analytical grade reagent (Lachema) was used. Crystals of 0.7 mm prevailed. The decomposition was carried out in the same furnace as the decomposition of sodium disulphite. Carbon dioxide and water were carried away with nitrogen at a rate of 180 ml/min and trapped in the same way as in case of $CaCO_3$.

RESULTS AND DISCUSSION

Kinetic curves were constructed as the dependence of degree of decomposition (η) on time. The degree of decomposition is defined as the ratio of the amount of gas liberated to the amount of gas which can be liberated altogether according to a corresponding equation.

Redox Disproportionation of Ferrous Sulphate

An example of kinetic curves is in Fig. 2. The curves have an S shape with a very short induction period. The sample attained a given temperature within 4 − 5 minutes

after inserting into the heated furnace. Therefore it can be judged that this short induction period was caused above all by a time difference among inserting the sample into furnace, heating the sample to the given temperature and the beginning of the absorption of SO_2. With samples containing bound water, the dehydration process preceding the disproportionation shares in the induction period, too. When determining the rate constants, the induction period was neglected; the way of converting the found kinetic curves to the kinetic curves of the zero-order reactions is illustrated in Fig. 2. During decomposition, the SO_3 evolution was observed, too. The amount of SO_3 formed was determined always at the end of experiment from a mass balance; the results are not presented here. Calculated degrees of decomposition higher than 1·00, which were often found, were caused by partial decomposition of $Fe_2(SO_4)_3$ and by establishing the equilibrium $SO_3 \rightleftarrows SO_2 + \frac{1}{2} O_2$. This simultaneously occurring reaction was not taken into account for calculating the rate constant. In spite of the fact that the evolving of SO_3 was observed (according to fumes) as a rule even at the beginning of decomposition, most SO_3 was formed probably only by de-
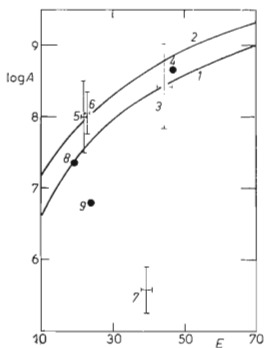

FIG. 1

Relation between Frequency Factor A and Activation Energy E (kcal/mol)

1 Calculation from Eq. (*11*) for temperatures at which $\log k_0 = -3$; 2 construction from values A determined by graphical extrapolating straight lines (*13*) to $1/T = 0$; experimental points: 3 $FeSO_4$, 4 $FeSO_4$ ref.[11], 5 $Na_2S_2O_5$, 6 $KHCO_3$, 7 $CaCO_3$. 8 $(NH_4)_2$.HPO_4 ref.[10], 9 $Mg(OH)_2$ ref.[12].
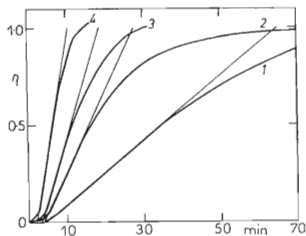
FIG. 2

Kinetics of $FeSO_4$ Disproportionation

Sample No 1, weighed portion 0·15 g, N_2 rate of flow 0·3 l/min, *1* 545, *2* 565, *3* 585, *4* 610°C.

composing the primarily formed $Fe_2(SO_4)_3$; considering that the starting rate (with an exception of induction period) was measured, the determination of SO_2 formed according to Eq. (A) could be influenced only little by the $Fe_2(SO_4)_3$ decomposition.

The Arrhenius relation was established for different conditions of measuring to find the effect of the mass of sample, kind of sample and flow rate of nitrogen. In Table I, the calculated activation energies and frequency factors are given. From the results it follows that the flow rate of nitrogen and kind of sample had no influence. It is possible to state a certain effect of weighed portion which seems, however, not to be substantial. From the Arrhenius dependence comprising all experimental points it follows $E = 44.5 \pm 2.2$ kcal/mol, $A = 8.43 \pm 0.59$. This result is plotted in Fig. 1; it corresponds to the theory. It was substituted $5 . 10^{18}$ m^{-2} for M into Eqs (11) and (13), which is an estimation of the number of Fe^{2+} ions per 1 m^2 of the crystal plane with the largest planar concentration of ions on the basis of ionic radii of Fe^{2+} and O^{2-}. It appeared that the value of M for different substances did not differ very much (the compounds and their 10^{-18}M are as follows: $CaCO_3$ 4.1, $Na_2S_2O_5$ 3.8, $KHCO_3$ 5.5) and therefore the results for all substances were compared with the

TABLE I

Measurement of Kinetics of Thermal Decomposition of Solid Substances in Nitrogen Atmosphere

Substance	Weighed portion g	Rate of flow 1/min	Temperature range °C	Number of measurements	log A^a	E^a kcal/mol
$FeSO_4$ No 2	0.15	0.30	477—609	10	8.66 ± 0.42	45.4 ± 1.6
No 2	0.075	0.30	490—580	7	10.44 ± 0.89	51.4 ± 3.3
No 1	0.15	0.15	506—610	6	8.66 ± 0.85	46.1 ± 3.2
No 1	0.15	0.30	525—610	5	7.02 ± 0.79	39.3 ± 3.0
No 2	0.075	0.30	477—609	17	9.28 ± 0.59	47.4 ± 2.2
	0.15					
No 1	0.15	0.15; 0.30	506—610	11	8.34 ± 0.82	44.6 ± 3.1
$FeSO_4{}^b$	—	—	—	28	8.43 ± 0.59	44.5 ± 2.2
$CaCO_3$	0.15	0.24	540—740	6	5.58 ± 0.32	39.4 ± 1.4
$Na_2S_2O_5{}^c$	0.10	0.10—0.24	138—193	11	9.24 ± 0.50	24.4 ± 1.0
$Na_2S_2O_5{}^d$	0.10	0.12—0.23	144—194	11	7.68 ± 0.22	21.6 ± 0.5
$Na_2S_2O_5{}^b$	—	—	—	22	8.00 ± 0.50	22.1 ± 1.0
$KHCO_3$	0.13—0.22	0.17—0.20	124—191	5	8.05 ± 0.30	22.7 ± 0.6

^{a} Root mean square deviation. ^{b} All measurements. ^{c} Sample in 5 g porcelain boat; atmosphere N_2, air. ^{d} Sample in 0.1 g glass boat; atmosphere N_2, air.

theoretical relation for $M = 5 . 10^{18} \, m^{-2}$ (Fig. 1). The agreement with theory supports the view that the rate of reaction was, in the given experimental arrangement, controlled by one elementary chemical process, *e.g.*

$$Fe^{2+} + SO_4^{2-} \rightarrow Fe^{3+} + SO_4^{3-} \qquad (E)$$

which can be followed by rapid consecutive reactions

$$SO_4^{3-} \rightarrow O^{2-} + SO_3^- , \qquad (F)$$

$$2 \, SO_3^- \rightarrow SO_4^{2-} + SO_2 . \qquad (G)$$
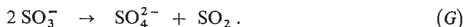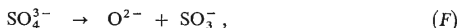
Activation energy of disproportionation is larger than the reaction enthalpy of reaction (A) calculated from the data presented in ref.[7] $(\Delta H_{800} = 12 \cdot 1 \, kcal/mol \, FeSO_4)$.

Decomposition of Calcium Carbonate

Kinetic curves have an S shape with very short induction period whose cause can be explained in the same way as with disproportionation of $FeSO_4$. The results are presented in Table I and in Fig. 1. Activation energy $E = 39 \cdot 4 \pm 1 \cdot 4 \, kcal/mol$ corresponds to the reaction enthalpy of reaction (B) $(\Delta H = 40 \, kcal/mol, ref.[3])$ and does not conform to the theoretical relation (Fig. 1); a reason for it is evidently the unfulfilled condition of irreversibility of the reaction.

Decomposition of Sodium Disulfite

Kinetic curves exhibit an S shape again with a very short induction period (3 min for the 5 g boat and 1 min for the 0·1 g one). It was found that the composition of atmosphere (nitrogen or air) has no effect on the decomposition kinetics according to Eq. (C). The measurements with the light boat conform to the theory better than those with the heavy one. The constants of the Arrhenius equation calculated on using all experimental points are plotted in Fig. 1. The agreement with theory is satisfactory. Activation energy $E = 22 \cdot 1 \pm 1 \cdot 0 \, kcal/mol$ is larger than the only in an older literature given reaction enthalpy (De Forcrand[8], $\Delta H = 18 \cdot 8 \, kcal/mol$). It was proved by the X-ray structural analysis that sodium sulphite was a solid product of decomposition in nitrogen atmosphere. Contingent oxidation reactions when decomposing sodium disulphite in air were not studied; as far as the oxidation occurs, evidently only sodium sulphite, *i.e.* the product of decomposition, takes part in it, so that the oxidation with oxygen from air does not influence the kinetics of decomposition according to Eq. (C).

Decomposition of Potassium Bicarbonate

Kinetic curves were again of an S shape with an induction period which lasted 1 h and got shorter rapidly with temperature (3 min at 191°C). When determining the rate constants, it was proceeded in the same way as in the preceding cases. The relation between A and E corresponds to the theory (Fig. 1); in this case, however, it is not supported because it was found by microscopic investigation that the decomposition did not take place in whole volume of crystal. Thus, it is probably the question of an incidental elimination of deviations from the theory owing to an action of nucleation and the displacement of phase boundary. Activation energy 22.7 ± 0.6 kcal/mol is apparently lower than reaction enthalpy corresponding to the reaction (D) for which[9] $\Delta H = 31.46$ kcal/mol. As activation energy cannot be lower than reaction enthalpy, it means that the controlling elementary process is not, probably, the formation of molecules of H_2O and CO_2 but the formation of activated state from one anion CO_3H^- so that in this case it is necessary to compare the activation energy with the half value of reaction enthalpy corresponding to Eq. (D); then the activation energy is larger than the reaction enthalpy.

Results of Measurements of Other Authors

The results of measurements of the decomposition kinetics of solid substances presented in the literature do not often contain the values of frequency factor, which makes it impossible to compare these results with theory. Many published kinetic measurements have been carried out by means of the thermogravimetric method with which suitable conditions do not exist for rapid removing the gaseous reaction products out of samples so that back reactions appear expressively; it makes unable to interpret the results as decomposition reactions controlled by one elementary chemical process. A relatively good agreement was found in case of the decomposition of $(NH_4)_2HPO_4$ on fluidized heating[10], disproportionation of $FeSO_4$ (ref.[11], from several results of the measurement obtained under different conditions, the result satisfying best the theory is plotted in Fig. 1) and decomposition of $Mg(OH)_2$ (ref.[12]).

CONCLUSION

On using the simplified model which presupposes the simultaneous course of reaction controlled by one elementary chemical process in entire crystal, the possibility was proved, in terms of simple decomposition reactions, of combination of the Planck law for black-body radiation with energy fluctuations in a crystal. The application of the approach described to the decomposition of other solids and of large crystals as well, for which the surface reaction and the displacement of phase boundary to the inside of crystal is characteristic, will be a matter of further study.

LIST OF SYMBOLS

A	frequency factor of the Arrhenius equation (s^{-1})
η	degree of decomposition
ν_f	frequency factor in Eq. (1) (s^{-1})
ν	frequency (s^{-1})
ν_1	lowest frequency satisfying relation (2) (s^{-1})
ν_{mean}	mean frequency defined by relation (7) (s^{-1})
c	velocity of light in vacuum $(m\,s^{-1})$
E	measured activation energy $(J\,mol^{-1})$ or $(kcal\,mol^{-1})$
$\Delta E^{\neq}$	change in internal energy connected with formation of 1 mol of activated complex $(J\,mol^{-1})$
h	Planck's constant $(J\,s)$
k	Boltzmann's constant $(J\,K^{-1})$
k_1	rate constant (s^{-1})
k_0	rate constant of zero-order reaction (s^{-1})
M	number of structural units capable of reaction (*e.g.* pairs of ions) on 1 m^2 plane of crystal (m^{-2})
M_1	minimum number of unreacted structural units on 1 m^2 crystal plane at which every quantum of energy defined by relation (2) still reacts (m^{-2})
N_A	Avogadro's number (mol^{-1})
n	number of molecules
$\bar{n}$	number of molecules on unit area in Eq. (1)
R	gas constant $(J\,K^{-1}\,mol^{-1})$
S	surface of boundary between decomposing solid substance and solid product of decomposition in Eq. (1)
s	entropy factor in Eq. (1)
T	temperature (K)
U	potential power of internal fluctuations of energy corresponding to frequency ν_1 and higher electromagnetic wave motion in crystal plane of 1 m^2 area $(J\,s^{-1}\,m^{-2})$
Y	number of energy quantums per second in 1 m^2 crystal plane satisfying relation (2) $(s^{-1}\,m^{-2})$

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