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INTERCONNECTION OF HEAT AND MECHANICAL ENERGY IN THE DESTRUCTION OF MATERIALS

Abstract. The destruction of solid materials is possible only due to heat exposure at the melting temperature. However, at low temperatures, the destruction may be achieved by mechanical energy impact which is supplemented to the thermal energy of the mill charge. The latter is described by the Boltzmann distribution, which may be applied to a solid state. In the framework of this distribution we can determine the probability of overcoming any energy barrier, taking into account thermal energy of the chaotic motion of particles.

On this basis, a formula to calculate the probability of destruction of matter by the summing action of thermal and mechanical energy was obtained. This ensures the relative decrease in the E_a activation barrier.

Keywords: thermal energy, mechanical energy, interconnection, destruction, Boltzmann distribution, probability theory, activation factor, grinding.

Introduction

It is known, that the destruction of solid materials is possible without mechanical interaction only due to thermal energy at the melting temperature. The same effect can be achieved by supplementing the existing heat energy material by mechanical impact at lower temperatures. This can be proved by means of Boltzmann distribution (energy spectrum) on the kinetic energy of the random motion of particles, and it is applicable to the solid state, as shown in the book of M.A. Leontovich [1].

Equal distribution of particles on kinetic energy of chaotic (thermal) motion depending on the temperature was established by Boltzmann in the following form [2]

$$P_i = N_i / N = \exp(-\varepsilon_i / kT) / \sum_{i=1}^m \exp(-\varepsilon_i / kT), \quad (1)$$

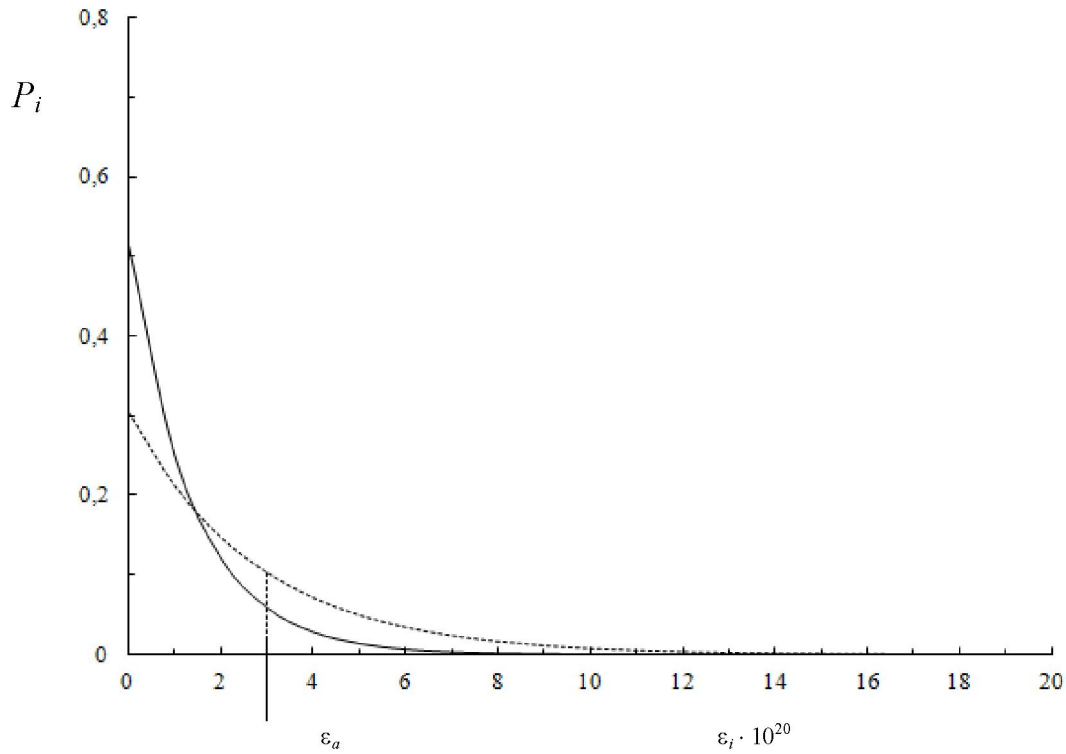
where P_i and N_i – fraction and number of particles with energy, ε_i ; N – total number of particles; k – Boltzmann's constant (named by Max Planck [2]); m – the number of considering energy levels. Magnitude P_i can be interpreted as probability detection of energy particles ε_i .

One of the properties of this distribution is the inhibition on the greater population of the future level of energy in comparison with the previous condition on

$P_{i+1} \leq P_i$. Another feature is to increase the levels of uneven settlement with increasing temperature. Thus, during 0 K, the first level is full, and during $T \rightarrow \infty$ full settlement of all levels of uniformity can be reached $P_i = 1/m$ и $m = N$ [3-5]. Such distribution for two arbitrary temperatures is given on Figure 1.

It has non-increasing character, in other words, the following condition is preserved $P_{i+1} \leq P_i$. With the rise of the temperature, distribution becomes more even (at $T \rightarrow \infty$ distribution becomes almost horizontal and coincides with the x axis). In all cases, the following condition is preserved

$$\sum_{i=1}^{m \leq N} P_i = 1. \quad (2)$$



P_i – fraction of particles, which have energy $\varepsilon_i \pm \Delta\varepsilon/2$, J; $\Delta\varepsilon$ – variability interval ε_i (in this case $\Delta\varepsilon = 10^{-20}$ J); ε_i – average energy of particle on i energy level, J. Solid line for temperature 1000 K, dotted line for 2000 K. ε_a – potential barrier

Figure 1 – Boltzmann distribution (energy spectrum)

In turn, the restriction $m \leq N$ is determined by the number of considering energy levels cannot exceed the number of holders of this feature of their distinctiveness, in other words, the number of particles [5].

In order to determine the fraction of particles which have energy more or less than potential barrier ε_a , it is necessary to sum the distribution of probabilities P_i which is higher that barrier ε_a :

$$P_a = \sum_a^m \exp(-\varepsilon_i/kT) / \sum_1^m \exp(-\varepsilon_i/kT), \tag{3}$$

where a – the number of energy levels corresponding to the activation energy. In order to provide certainty of number a , a whole-number value based on the following ratio should be set

$$\Delta\varepsilon = \varepsilon_a / a, \tag{4}$$

where $\Delta\varepsilon$ – regular energy interval – variation step ε_i .

For a more exact expression P_a , we have to switch from the discrete energy distribution to continuous one, or, to switch from summation to integration. First of all, the numerator and denominator of the fraction (3) are multiplied by $\Delta\varepsilon$ and this factor is put under the summation sign:

$$P_a = \sum_a^m \Delta\varepsilon \exp(-\varepsilon_i/kT) / \sum_1^m \Delta\varepsilon \exp(-\varepsilon_i/kT). \tag{5}$$

when $m \rightarrow \infty$ and $\Delta\varepsilon \rightarrow d\varepsilon$, the transition into integral form is provided

$$P_a = \int_{\varepsilon_a}^{\infty} \exp(-\varepsilon/kT) d\varepsilon \bigg/ \int_0^{\infty} \exp(-\varepsilon/kT) d\varepsilon. \quad (6)$$

This expression reveals the geometric meaning of the function P_a (see Fig. 1): it is equal to the area under the curve $P = f(\varepsilon)$ (this area is the integral of this function) on the right side from ε_a to the area under the whole curve. It is obvious from Fig. 1 that with the rise of temperature, the area under the curve on the right side from ε_a increases, on the left side decreases, that is why the fraction of over barrier particles must increase.

From mathematical point of view, this result is obtained after taking integrals. Thus, primitive function for indefinite integral $\int \exp[-\varepsilon/(kT)] d\varepsilon$ is following

$$F = -kT \exp[-\varepsilon/(kT)] + const. \quad (7)$$

When taking improper integrals in (6) the integration constant is reduced, so integral in the numerator is

$$\int_{\varepsilon_a}^{\infty} \exp[-\varepsilon/(kT)] d\varepsilon = \left[-kT \exp[-\varepsilon/(kT)] \right]_{\varepsilon_a}^{\infty} = kT \exp[-\varepsilon_a/(kT)]. \quad (8)$$

The integral in the denominator is

$$\int_0^{\infty} \exp[-\varepsilon/(kT)] d\varepsilon = \left[-kT \exp[-\varepsilon/(kT)] \right]_0^{\infty} = kT. \quad (9)$$

In general, desired expression is

$$P_a = \exp[-\varepsilon_a/(kT)], \quad (10)$$

resulting the need to increase the fraction of over barrier particles with increasing temperature.

This expression is used as a constituent of a constant velocity even in the Arrhenius equation approximation, and then in terms of more stringent expressions of formal kinetics [6]. No less important is the integral (9), because it makes sense for average integral thermal energy of the particle at a temperature T , with directly comparison of energy barrier ε_a in formula (10). In terms of moles, this formula has the form of

$$P_a = \exp[-E_a/(RT)], \quad (11)$$

of which RT acquires a meaning of average integral heat energy mole of a substance at a temperature T .

Generally, according to the theorem of the average value of function, its actual, mathematically strict value can be determined as the average integral [7]. Therefore, we will call the RT value as average thermal energy.

Detailed consideration of the energy behavior of individual particles in the framework of the Boltzmann distribution can be understood as the microscopic approach; taking into account the average thermal energy as a macroscopic one. Apparently, in this connection of the two extremes, lies enduring value of such representation of complex systems and the possibility to solve specific problems [8], which comprise the issue of adequate displaying the impact of mechanical energy to the destruction of materials.

Interpretation of collapsibility of materials under the summing action of thermal and mechanical energy

In our opinion, the main reason for failure of solution for this problem, considered in this paper [9], is excessive direct comparison of mechanical energy E_{mec} with bound energy of particles E_b , which consists of the subtraction of the first from the second one, for various options for activation destruction

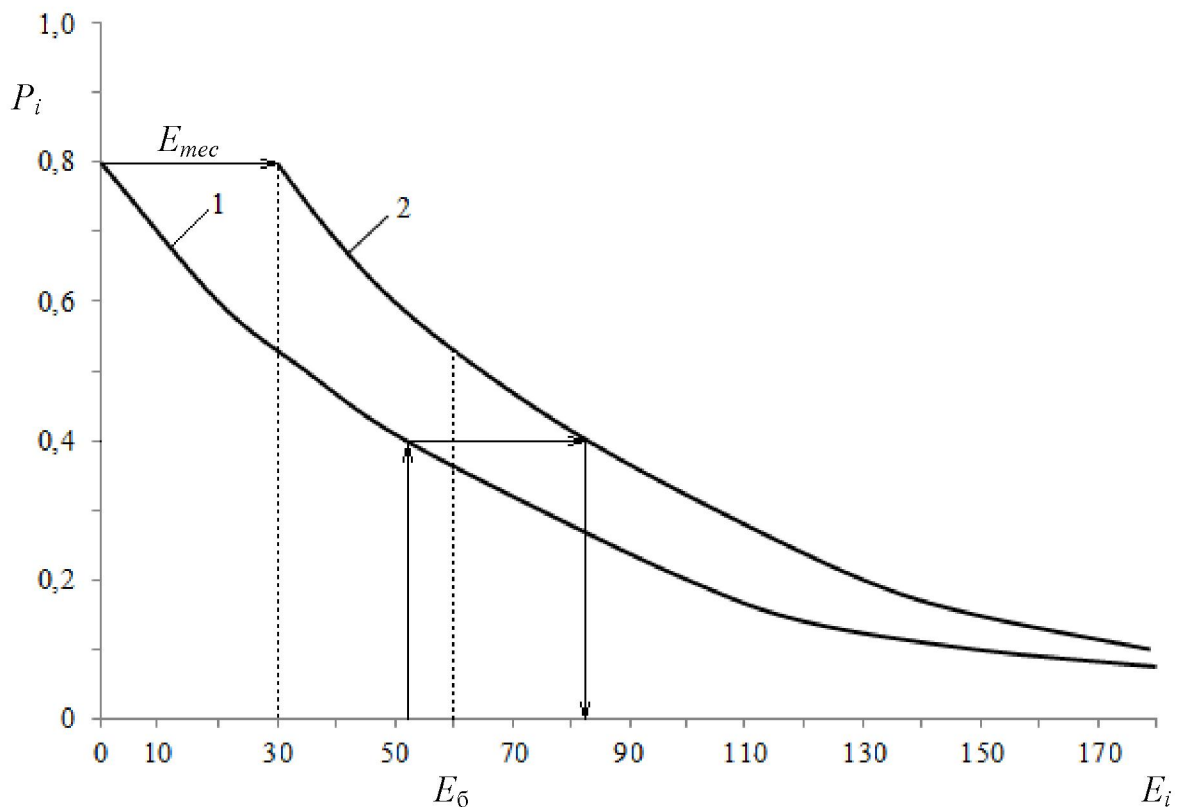
$$P_a = \exp\left(-\frac{E_b - E_{mec}}{RT}\right). \tag{12}$$

Here, during increasing of mechanical energy, the probability of destruction of structure increases, however $E_{mec} > E_b$, which in real terms of destruction may be the norm, but values might be senseless $P_a > 1$. In addition, during such expression of activation factor, thermal and mechanical energy are opposed to each other.

Apparently, considering way of expression of activation energy is taken from the molecular kinetics, which aim is the reduction of activation energy through the use of catalysts.

Meanwhile, during impact of mechanical energy on substance, it is added to the system of thermal energy rather than subtracted from the energy of the particles which may be due to overall impact of thermal and mechanical energy to the substance.

In terms of non-equilibrium addition of mechanical energy, this can be represented as a shift of all energy distribution to the same value for all particles of mechanical energy due to the elastic properties of crystal (Fig. 2).



E_i – energy of particles; E_b – barrier energy, equal to energy of destruction activation E_a ;
 E_{mec} – mechanical energy; P_i – fraction of particles with E_i energy before impact (1)
 with energy $E_i + E_{mec}$ in moment of mechanical impact (2).

Figure 2 – Shift of particles energy by Boltzmann distribution during mechanical impact (per mole). The arrows indicate an instantaneous increase in arbitrary particle energy

We cannot exclude a partial relaxation of the system, accompanied by raise of temperature. The probability to destruct some energy barrier E_b will increase not by absolute, but by relative lowering of the

barrier due to the increase of the total energy of all the particles, resulting over barrier particles (indicated by the arrows movement).

Thus, according to physical reasons, the destruction probability should be expressed as counteracting result of heat and mechanical energy amount to activation barrier energy of substance destruction:

$$P_a = \exp\left(-\frac{E_a}{RT + E_{mec}}\right). \quad (13)$$

Here, unlike (12), the appearance of senseless results is excluded for any RT and E_{mec} , and the provision is guaranteed $0 \leq P_a \leq 1$, while $E_{mec} \gg RT$ the role of thermal energy becomes insignificant.

Since the dimension RT , like E_a , is expressed by specific molar value (J/mol), it is necessary to bring the dimensions and mechanical energy. It's enough to take into account the number of moles in depleting substance and include the value of the mechanical energy to this number:

$$P_a = \exp\left(-\frac{E_a}{RT + \frac{E_{mec}M}{m}}\right), \quad (14)$$

where m – mass of depleting substance, kg; M – its molar mass, kg/mol; E – applying mechanical energy, J.

In fact, all the calculations are valid for any type of influencing energy – sound, radiant (especially, laser), but the most common is the blow energy. We show this in the example of the application of the formula (14) in the new theory of ore reduction, more adequately reflects the probabilistic nature of the process [10-16].

The role of the activation factor in the probabilistic theory of reduction

In this theory, the reduction speed is considered as a production of the probabilities of successive events of joint presence of grinding and grinded bodies in the extent of their randomized mixture (concentration factor, P_{conc}), their spatial compatibility – contact (steric factor, P_{st}), the direct impact of the grinding bodies in the mill material (activation factor P_a) at periodic sustainability of these events (frequency factor, Z , c^{-1}):

$$V = Z \cdot P_{конц} \cdot P_{ст} \cdot P_a. \quad (15)$$

All factors are revealed through specifications on mills, physical constants and operational parameters of grinding process, and also through the blow energy of ball hitting the grain. Thus, the disclosure activation factor (14) leads to the formula

$$P_a = \exp\left[-\frac{E_a}{RT + MgD(\gamma_{uu}/\gamma_3)(d_{uu}/d_j)^3}\right], \quad (16)$$

where E_a - activation energy, adopted for model calculations in equal heat of quartz fusion (the main rock-forming mineral ore) 9170 J/mole; R – universal gas constant, equal to 8,31441 J/(mole·K); T – absolute temperature, equal to room temperature, 298 K; M – molecular weight of quartz, 0,0601 kg/mole; g – gravitation acceleration, 9,807 m/sec²; D – bottom diameter of mill, for model calculations taken from industrial mill characteristics equal to 3,36 m; γ_{uu} and γ_3 - density of material and ore,

accordingly 7874 and 2650 kg/m³; d_b – ball diameter, equal to 0,06 m in average; d_j – size of grains of j fraction.

The impact energy is taken into account through the equivalent to its potential energy of the ball, weight m_u , during fall from a height $h = D$ [14] by the formula

$$E_{mec} = m_b g h. \tag{17}$$

Therefore, it follows from the formula (16) that with decreasing of grain size and increasing of the ball diameter, the destructibility of grains sharply rises. However, this counteracts by the steric (shield factor), which according to geometric ratio of the ball and the grain gets expression

$$P_{cr} = 4 \left[\frac{d_j}{d_u} - \left(\frac{d_j}{d_u} \right)^2 \right]. \tag{18}$$

Here, in contrast, the magnitude of this factor of balls is reduced during the same change in the grain size. Their combined effect is illustrated in Figure 3.

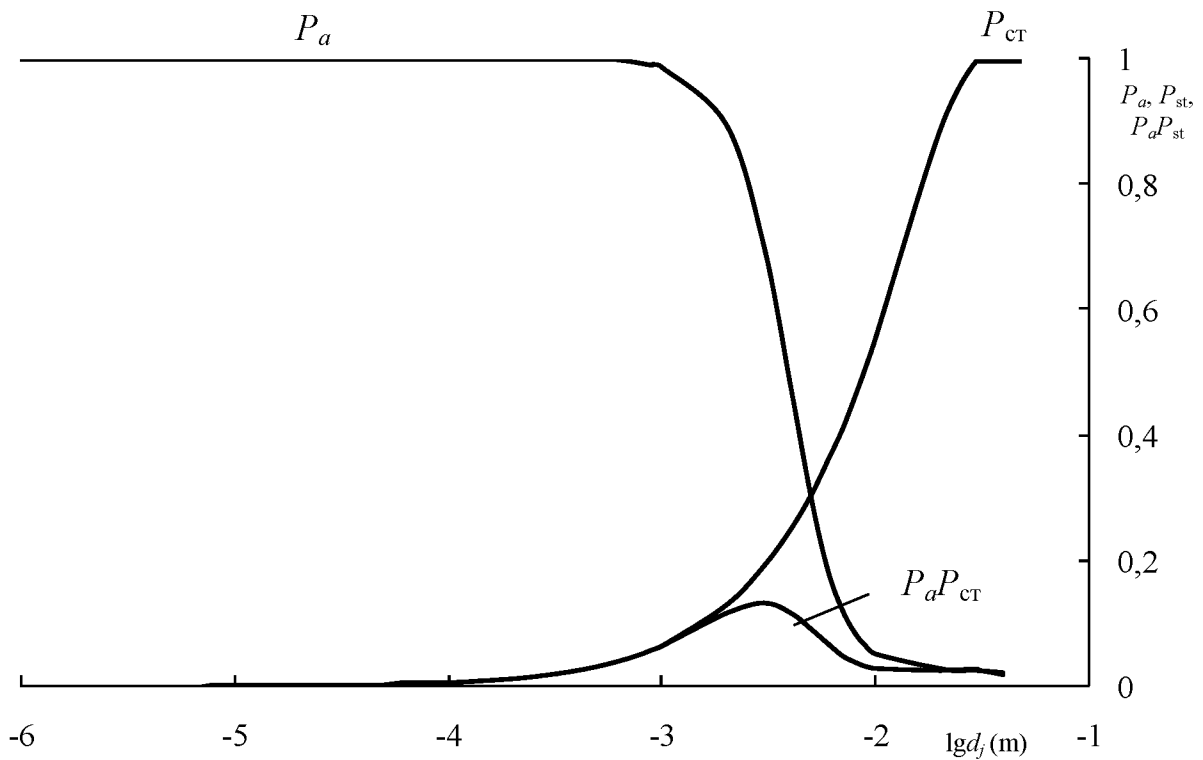


Figure 3 – The dependence of activation and steric factors and their joint effect in each cycle of collisions from the grain size

The findings prove the dominance of the steric factor in the total destruction of all insignificant small classes ranging from 10⁻⁶ to 10⁻⁴ with all the destructive power of the direct impact of the ball to the grain. A significant increase in degradability by unfastening of steric factor begins only with 10⁻³ m, but the weakening and activation leads to the formation of degradability on the level of 13.3% for the grain size of 3 mm. Outside this zone, the energy of ball falling spent literally wasted either due to misses in the fine grains from the "dead" (screened) area, or because of a lack of power hitting to break the larger grains.

For the first time in the framework of probability of grinding theory, the extremely low energy

efficiency of the process that requires a minimum 90% of the costs of mining and metallurgical cycle is explained. The result can be considered as further evidence of the enduring value of the statistical distribution (energy spectrum) of Boltzmann, still preserving its topicality for various fields of science and practice [10].

Conclusion

Boltzmann distribution enables to determine the probability of overcoming any energy barrier by the thermal energy of chaotic motion of particles. This effect can be supplemented by taking into account the applied mechanical energy through summing it to heat. In this case the resulting formula is a probability of a substance destruction at a total impact of heat (RT) and mechanical (E_{mec}) energy

$$P_a = \exp\left(-\frac{E_a}{RT + E_{mec}}\right)$$

and provides a relative decrease in the activation barrier E_a . This activation factor is used in the probabilistic theory of materials grinding, and the reason of low energy efficiency of this high input process is revealed.

REFERENCES

- [1] Malyshev V.P. One World. Spontaneity. Controllability. Freedom. Parasitism. M.: Nauchnyj mir, **2012**, 216 p. (in Russ.).
- [2] Bol'cman L. Selected works. The molecular-kinetic theory of gases. Thermodynamics. Statistical mechanics. Radiation Theory. General questions of physics. M.: Nauka, **1984**, 590 p. (in Russ.).
- [3] Malyshev V.P. Fundamentals of thermodynamics of matter at an infinitely high temperature. Alma-Ata: Nauka, **1986**, 64 p. (in Russ.).
- [4] Nurmagambetova A.M., Malyshev V.P., Mamjachenkov S.V. *Vestnik UGTU-UIPI*, **2004**, 5(35), 215-218. (in Russ.).
- [5] Malyshev V.P. Probabilistic and deterministic mapping. Almaty: Fylym, **1994**, 376 p. (in Russ.).
- [6] Jemanujel' N.M., Knorre D.G. Chemical Kinetics Course. Textbook for chemical faculties. Ed. 3rd, revised and additional. M.: Vysshaja shkola, **1974**, 400 p. (in Russ.).
- [7] Bronshtejn M.N., Semendjaev K.A. Handbook of mathematics for engineers and technical colleges students. 13th ed., revised. M.: Nauka, **1987**, 544 p. (in Russ.).
- [8] Chertin'jani K. The theory and applying of the Boltzmann equation. Trans. from English. M.: Mir, **1978**, 496 p. (in Russ.).
- [9] Hodakov G.S. Physics of grinding. M.: Nauka, **1972**, 240 p. (in Russ.).
- [10] Malyshev V.P. *Obogashhenie rud*, **1995**, 4-5, 4-14. (in Russ.).
- [11] Malyshev V.P., Turdukozhayeva (Makasheva) A.M., Kajkenov D.A. *Obogashhenie rud*, **2012**, 4, 29-35. (in Russ.).
- [12] Malyshev V.P. *Jenciklopedija inzhenera-himika*, **2013**, 9, 54-59; 10, 56-60; 11, 44-52. (in Russ.).
- [13] V.P. Malyshev, A.M. Turdukozhayeva. *Journal of Materials Science and Engineering A*, **2013**, 2, 131-144. (in Eng.).
- [14] Malyshev V.P., Turdukozhayeva A.M., Ospanov E.A., Sarkenov B. Evaporation and boiling simple substances. M.: Nauchnyj mir, **2010**, 304 p. (in Russ.).
- [15] Zhuhovickij A.A., Shvareman L.A. Physical chemistry: textbook for high schools - 4th ed., revised and additional. M.: Metallurgija, **1987**, 688 p. (in Russ.).
- [16] Malyshev V.P., Makasheva A.M., Zubrina Ju.S. *Obogashhenie rud*, **2016**, 1, 22-26. (in Russ.).

ЛИТЕРАТУРА

- [1] Мальшев В.П. Единый мир. Стихийность. Управляемость. Свобода. Паразитизм. – М.: Научный мир, 2012. – 216 с.
- [2] Больцман Л. Избранные труды. Молекулярно-кинетическая теория газов. Термодинамика. Статистическая механика. Теория излучения. Общие вопросы физики. – М.: Наука, 1984. – 590 с.
- [3] Мальшев В.П. Основы термодинамики вещества при бесконечно высокой температуре. – Алма-Ата: Наука, 1986. – 64 с.
- [4] Нурмагамбетова А.М., Мальшев В.П., Мамяченков С.В. Энергетические аспекты распределения Больцмана // *Вестник УГТУ-УПИ*. – 2004. – № 5(35). – С. 215-218.
- [5] Мальшев В.П. Вероятностно-детерминированное отображение. – Алматы: ФЫЛЫМ, 1994. – 376 с.
- [6] Эмануэль Н.М., Кнорре Д.Г. Курс химической кинетики. Учебник для химических факультетов. Изд. 3-е, перераб. и доп. – М.: Высшая школа, 1974. – 400 с.

- [7] Бронштейн М.Н., Семендяев К.А. Справочник по математике для инженеров и учащихся втузов. 13-е изд., исправленное. – М.: Наука, 1987. – 544 с.
- [8] Чертиньяни К. Теория и приложения уравнения Больцмана. Пер. с англ. – М.: Мир, 1978. – 496 с.
- [9] Ходаков Г.С. Физика измельчения. – М.: Наука, 1972. – 240 с.
- [10] Мальшев В.П. Новый аспект в теории измельчения руд и управления этим процессом // Обогащение руд. – 1995. – № 4-5. – С. 4-14.
- [11] Мальшев В.П., Турдукожаева (Макашева) А.М., Кайкенов Д.А. Развитие теории измельчения руд на основе молекулярной теории соударений и формальной кинетики последовательных реакций // Обогащение руд. – 2012. – № 4. – С. 29-35.
- [12] Мальшев В.П. Молекулярный шарм и гремящее торнадо барабанных шаровых мельниц // Энциклопедия инженера-химика. – 2013. – № 9. – С. 54-59; – № 10. – С. 56-60; – № 11. – С. 44-52.
- [13] V.P. Malyshev, A.M. Turdukozhaeva. What Thunder There and is not Heard When Using Ball Mills? // Journal of Materials Science and Engineering A. – 2013. – V. 3. – № 2. – P. 131-144.
- [14] Мальшев В.П., Турдукожаева А.М., Оспанов Е.А., Саркенов Б. Испаряемость и кипение простых веществ. – М.: Научный мир, 2010. – 304 с.
- [15] Жуховицкий А.А., Шварцман Л.А. Физическая химия: Учебник для вузов – 4-е изд., перераб. и доп. – М.: Металлургия, 1987. – 688 с.
- [16] Мальшев В.П., Макашева А.М., Зубрина Ю.С. Влияние взаимного противодействия стерического и активационного факторов на эффективность процесса измельчения // Обогащение руд. – 2016. №1. – с. 22-26.

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МАТЕРИАЛДАРДЫҢ БҮЛІНУІ КЕЗІНДЕГІ МЕХАНИКАЛЫҚ ЖӘНЕ ЖЫЛУЛЫҚ ЭНЕРГИЯНЫҢ ӨЗАРА БАЙЛАНЫСЫ

Аннотация. Тек еру температурасындағы жылу әсері есебінен қатты материалдардың бүлінуі мүмкін. Алайда төмен температурада бүліну механикалық өзара байланыс энергиясының көмегімен жетуі мүмкін, және де ол ұсақталған материалдың жылулық энергиясына толықтырылады. Қатты күйге қолдануға болатын Больцманның таратуы ең соңғы болып жазылады. Осы бөлудің аясында бөлшектердің ретсіз қозғалуындағы жылулық энергияны ескере отырып, кез келген энергетикалық кедергіден өту ықтималдығын анықтауға болады.

Осы негізде заттектердің бүліну ықтималдылығын есептеу үшін формула шығарылған, ол жылулық және механикалық энергияның жалпы әсер етуін ескереді, осылайша E_a активация кедергісінің салыстырмалы төмендеуін қамтамасыз етеді.

Түйін сөздер: жылулық энергия, механикалық энергия, өзара байланыс, бүліну, Больцманның таратуы, ықтималдық теория, активациялық фактор, ұсақтау.

УДК 622.8

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ВЗАИМОСВЯЗЬ ТЕПЛОВОЙ И МЕХАНИЧЕСКОЙ ЭНЕРГИИ ПРИ РАЗРУШЕНИИ МАТЕРИАЛОВ

Аннотация. Разрушение твердых материалов возможно за счет только теплового воздействия при температуре плавления. Но при низких температурах разрушение может быть достигнуто с помощью энергии механического воздействия, которое дополняется к тепловой энергии измельчаемого материала. Последняя описывается распределением Больцмана, которое вполне можно применить к твердому состоянию. В рамках этого распределения можно определить вероятность преодоления любого энергетического барьера, учитывая тепловую энергию хаотического движения частиц.

На этой основе выведена формула для расчета вероятности разрушения вещества по суммарному воздействию тепловой и механической энергии. Тем самым обеспечивается относительное понижение барьера активации E_a .

Ключевые слова: тепловая энергия, механическая энергия, взаимосвязь, разрушение, распределение Больцмана, вероятностная теория, активационный фактор, измельчение.