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RESEARCH ARTICLE

A CONCEPT ON THERMAL EQUILIBRIUM ESTABLISHMENT TO BE WIDELY USED IN HEAT TREATING INDUSTRY AND OTHER TECHNOLOGICAL PROCESSES

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ABSTRACT

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Key words: Heating, Cooling,

Universal correlation, Fluctuations, Thermal equilibrium, Establishment, Physical meaning, Practical use. In the paper an universal correlation is proposed for calculating heating and cooling time of any steel part during its hardening. The equation contains Kondratjev form factor K, Kondratjev number Kn, average thermal diffusivity of a material and a function depending on how N - times core temperature of steel part differ from its initial temperature. It is shown that these parameters are enough to calculate recipes when heating and cooling the steel parts of any configuration. A tendency of thermal equilibrium establishment is considered which depends on size and configuration of objects, thermal diffusivity of a material and condition of cooling (heating) characterized by Kondratjev number Kn. The proposed generalized equation provides engineers with extremely simple and understandable parameters for calculating heating (cooling) soak time of any objects. According to proposed equation, the time of thermal equilibrium establishment is directly proportional to Kondratjev form factor K, inversely proportional to thermal diffusivity of material and Kondratjev number Kn and depends on accuracy of thermal equilibrium measurement.

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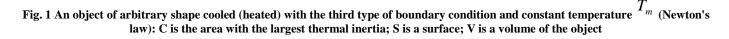
INTRODUCTION

When a system with a higher temperature is in contact with a lower temperature system, heat transfers to the lower temperature system. Systems are in thermal equilibrium when they reach the same constant temperature. Thermal equilibrium follows zeroth's law of thermodynamics. The zeroth law of thermodynamics states the following. When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other (NASA, 2015, Krichevskii, 1962, Buchdahl, 1966, Bailyn, 1994, Lucas, 2015). It means that sooner or later thermal equilibrium establishes within the finite period of time if in closed thermodynamic system temperatures are different. In physics, the thermal equilibrium is a basis for the next three laws of thermodynamics. In everyday practical activity people observe transition from one thermal equilibrium to another thermal equilibrium. Such transition occur in heat treating industry when objects are heated from room temperature to high temperature 800oC - 900°C to provide austenization and then cooled back to room temperature in liquids or air to produce hardening processes. In food industry products also are heated in furnaces and cooled in refrigerators to keep at a low temperature. As known, cryogenic industry needs exact determination of thermal equilibrium establishment. However, the classical theory of heat conductivity provides us with the exponential law of heating (cooling) which says that the thermal equilibrium establishes when time tends to infinity. Many scientists claim that there is no sense to consider thermal equilibrium in the frame of classical heat conductivity theory since thermal equilibrium never establishes, or establishes when $\ddagger = \infty$. It looks like there is a contradiction between main postulate of thermodynamics (zeroth law of thermodynamics) and classical heat conductivity theory. Just heat conductivity theory doesn't take into account thermal fluctuation, wave character of temperature distribution and free electrons in materials which transfer thermal energy for long distance. In statistical mechanics, thermal fluctuations are random deviations of a system from its average state that occur in a system at equilibrium. All thermal fluctuations become larger and more frequent as the temperature increases, and they disappear altogether as temperature approaches absolute zero.

Thermal fluctuations are a source of noise in many systems. The random forces that give rise to thermal fluctuations are a source of both diffusion and dissipation. Thermal fluctuations play a major role in phase transition and chemical kinetics. If one takes into account the temperature fluctuation, he will be able to determine final time of thermal equilibrium establishment. Also, if one considers hyperbolic heat conductivity equation, he will be able to see the wave character of temperature distribution. From the practical point of view, it makes sense to consider thermal equilibrium establishment when dimensionless temperature reduces 1000 times and approaches the processes of thermal fluctuations. These fundamental basics are discussed in detail below.

Regular thermal process

Assume that there is an object of any configuration with a surface S and volume V heated to initial temperature To which is cooled by the law of Newton represented by third kind of boundary conditions (see Fig. 1). One should determine the time when temperature T in area C is in thermal equilibrium with the cooling system.



As known, the parabolic heat conductivity differential equation is as follows:

$$\frac{1}{a}\frac{\partial T}{\partial t} = div(gradT)$$

$$\left[\frac{\partial T}{\partial n} + \frac{r}{3}(T - T_m)\right]_{S} = 0$$
(2)

$$T(x, y, z, 0) = T_0 = const$$

In 1926 well known mathematician Boussinesq proposed the general solution of Eq. (1) with the third type of boundary condition for objects of any configuration which was presented in form (4) and used by Kondratjev to develop theory on regular thermal mode (Kondratjev, 1954):

$$\frac{T - T_m}{T_0 - T_m} = \sum_{n=1}^{\infty} A_n U_n \exp(-m_n \ddagger)$$
(4)

 A_n are temperature amplitudes;

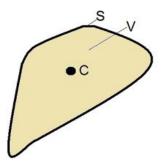
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 U_n are eigenfunctions dependent on coordinates which are known only for simple configurations.

The values m_n in exponent (see Eq. (4), according to Bussinesq, are arranged as:

$$m_1 < m_2 < m_3 \dots m_n < m_{m+1} \tag{5}$$

In view of inequities (5), in a very short time the process of cooling of a body of any shape will be described by just a simple exponent (Kondratjev, 1954, Kobasko, 2010):



(2)

$$_{''} = \frac{T - T_{m}}{T_{o} - T_{m}} = A_{1}U_{1}e^{-m_{1}\ddagger}$$

 $\ln_{"} = \ln(AU) - m^{\ddagger}$

$$\ln(T-T_m) - \ln(T_o - T_m) = -m^{\ddagger} + \ln(AU)$$

$$\ddagger = \left[\ln(AU) + \ln_{\pi_0}\right] \frac{1}{m}$$

$$_{m 0} = \frac{T_0 - T_m}{T - T_m}$$

Lykov (Lykov, 1967) provided a monograms for calculating time of regular thermal process establishment for different geometrical shapes. For cylindrical form the monogram is presented in Fig. 2.

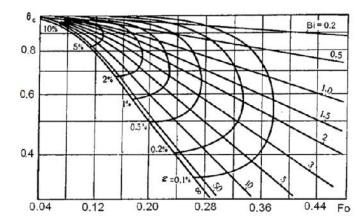


Fig. 2. The beginning of regular thermal process versus Fo, Bi, and an acceptable error of calculations $V_{(\%)}$ at the axis of a cylinder

Based on Eq (7) and regular thermal condition theory of Kondratjev, it has been proposed a generalized equation (8) for calculating cooling (heating) time of the objects of any configuration for condition of $0 \le Bi_V \le \infty$ (Kobasko, 1969):

$$\ddagger = \left[\frac{kBi_{V}}{2.095 + 3.867Bi_{V}} + \ln\left(\frac{T_{0} - T_{m}}{T - T_{m}}\right)\right]\frac{K}{aKn}.$$
(8)

The values of $2.095 + 3.867 Bi_v$ are responsible for irregular thermal process and were calculated for plate, cylindrical and spherical like forms which are presented in Fig. 3.

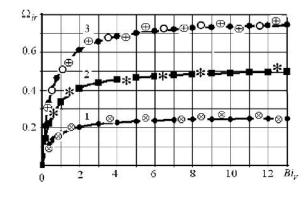


Fig. 3. Ω_{ir} versus generalized Biot number: 1- plate-shaped forms (round, squared and long plates); 2 - cylindrical - shaped forms (cylinder, prism, long hexagonal form); 3 - spherical - shaped forms ball, cube, finite cylinder with D = Z), (Kobasko, 1969)

(6)

(7)

Where BiV is generalized Biot number and is determined as:

$$BiV = \frac{\Gamma}{3}K\frac{S}{V}$$
(9)

Kn is Kondratjev number (see Table 1).

There is an universal interconnection between Kn and BiV numbers (see Fig. 4). Well known thermal scientist Lykov underlined that curves Kn = f(BiV) for different geometries like sphere, cube, cylinder, prism, plate and others forms (see Fig. 4) can be approximated by one curve which has analytical presentation (10)

$$Kn = \frac{Bi_V}{\left(Bi_V^2 + 1.437Bi_V + 1\right)^{0.5}}$$
(10)

Eq. (10) is an universal correlation of regular thermal condition theory of Kondratjev and is often presented as

$$Kn = \mathbb{E}Bi_V \tag{11}$$

where the non- smoothness criterion of temperature distribution $\mathbb{E}_{\text{along with}} = \frac{1}{\left(Bi_V^2 + 1.437Bi_V + 1\right)^{0.5}}$

$$\frac{T_{sf} - T_m}{\overline{T_V} - T_m} = \frac{1}{\left(Bi_V^2 + 1.437Bi_V + 1\right)^{0.5}}$$
(12)
Here $\overline{T_{sf}}$ is average surface temperature: \overline{T} is average volume temperature: T_m is medium temperature.

Table 1. Kondratjev coefficient K, S/V, K(S/V) depending on different shapes and sizes of solid bodies

Shape	Kondratjev coefficient K, m2	$\frac{S}{V}$, m-1	$K\frac{S}{V}$, m
Slab of thickness L	$\frac{L^2}{f^2}$	$\frac{2}{L}$	$\frac{2L}{f^2}$
Infinite cylinder of radius R	$\frac{R^2}{5.784}$	$\frac{2}{R}$	$_{0.346}R$
Infinite prism with sides of L	$\frac{L^2}{2f^2}$	$\frac{4}{L}$	$\frac{2L}{f^2}$
Cylinder of radius R and height Z	$\frac{\frac{1}{5.784}}{\frac{f^2}{R^2} + \frac{f^2}{Z^2}}$	$\left(\frac{2}{R} + \frac{2}{Z}\right)$	$\frac{2RZ(R+Z)}{5.784Z^2 + f^2R^2}$
Plate with sides L1, L2, L3	$\frac{1}{f^2\left(\frac{1}{L_1^2} + \frac{1}{L_2^2} + \frac{1}{L_3^2}\right)}$	$\frac{2(L_1L_2+L_1L_3+L_2L_3)}{L_1L_2L_3}$	$\frac{2(L_1L_2 + L_1L_3 + L_2L_3)L_1L_2L_3}{f^2(L_1^2L_2^2 + L_1^2L_3^2 + L_1^2L_3^2 + L_2^2L_3^2)}$
Sphere	$\frac{R^2}{f^2}$	$\frac{3}{R}$	0.304 <i>R</i>

Notes: L is thickness of slab, S is surface, V is volume, R is radius.

Practical use of generalized correlation

For heating and cooling time calculations is proposed a very simple equation (13) when using values E_{eq} from Table 2:

$$\ddagger_{eq} = E_{eq} \frac{K}{aKn} \tag{1}$$

When heating in industrial furnaces, average heat transfer coefficients (HTCs) can be calculated from Eq. (14).

(13)

$$\overline{\Gamma} = \Gamma_{conv} + c_0 v \left[\frac{\left(\frac{T_s}{100}\right)^4 - \left(\frac{T_{sf}}{100}\right)^4}{T_s - T_{sf}} \right]^4$$
$$c_0 = 5.67W \left(m^2 K^4\right).$$

Some results of calculations of average HTCs one can find in Ref. (Lienhard IV and Lienhard V, 2016).

						$Bi_V = 0.1$					
			0.7		0.5	E _{eq}			10	100	100
N Plate	1.5 0.44	2 0.73	2.5 0.96	3 1.14	3.5 1.29	4 1.43	4.5 1.54	5 1.65	10 2.38	100 4.64	1000 6.95
Cylinder	0.44	0.75	1.00	1.14	1.29	1.45	1.54	1.65	2.38	4.64 4.68	6.99
Sphere	0.55	0.81	1.04	1.10	1.37	1.51	1.62	1.73	2.46	4.72	7.02
Sphere	0.000	0.01	1101	1.22	1107	$Bi_V = 0.5$	1102	1.10	2.10		
						E_{eq}					
N	1.5	2	2.5	3	3.5	4	4.5	5	10	100	100
Plate	0.53	0.817	1.04	1.22	1.38	1.51	1.63	1.73	2.43	4.73	7.03
Cylinder	0.65	0.94	1.16	1.35	1.50	1.63	1.75	1.86	2.55	4.85	7.16
Sphere	0.78	1.07	1.29	1.47	1.62	1.76	1.88	1.98	2.67	4.98	7.28
						$Bi_V = 1$					
						E_{eq}					
Ν	1.5	2	2.5	3	3.5	4	4.5	5	10	100	100
Plate	0.57	0.86	1.08	1.27	1.42	1.55	1.67	1.78	2.47	4.77	7.07
Cylinder	0.74	1.03	1.25	1.44	1.59	1.72	1.84	1.94	2.64	4.94	7.24
Sphere	0.91	1.20	1.42	1.60	1.76	1.89	2.01	2.11	2.80	5.11	7.41
						$Bi_V = 2$					
						E_{eq}					
Ν	1.5	2	2.5	3	3.5	4	4.5	5	10	100	100
Plate	0.61	0.90	1.12	1.30	1.46	1.59	1.71	1.81	2.51	4.81	7.11
Cylinder	0.81	1.1	1.32	1.50	1.66	1.79	1.91	2.02	2.71	5.01	7.33
Sphere	1.01	1.30	1.52	1.71	1.86	1.99 $Bi_V = 5$	2.11	2.22	2.91	5.21	7.51
						E_{eq}					
N	1.5	2	2.5	3	3.5	— <i>eq</i> 4	4.5	5	10	100	100
Plate	0.63	0.92	1.14	1.32	1.48	1.61	1.73	1.83	2.53	4.83	7.13
Cylinder	0.86	1.15	1.37	1.55	1.71	1.84	1.96	2.07	2.76	5.06	7.36
Sphere	1.10	1.38	1.61	1.80	1.94	2.08	2.20	2.30	3.00	5.29	7.58
						$Bi_V = \infty$					
						$E_{_{eq}}$					
N	1.5	2	2.5	3	3.5	4	4.5	5	10	100	100
Plate	0.64	0.93	1.15	1.33	1.49	1.62	1.74	1.84	2.54	4.84	7.15
Cylinder	0.87	1.16	1.38	1.56	1.72	1.85	1.97	2.08	2.77	5.07	7.38
Sphere	1.11	1.39	1.62	1.80	1.95	2.09	2.20	2.31	3.00	5.30	7.6

Table 2. Coefficients	E_{eq} depending on dimensionless value "	which was decreased from 1.5 to 1000 times for different generalized Biot
		numbers BiV

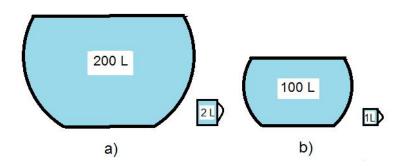
(14)

Names	T, oC	V	$\overline{r}_{,W/m2K}$
	840	0.65	230
Polished iron	900	0.65	270
	950	0.65	300
	840	0.8	275
Oxidized steel	900	0.8	325
	950	0.8	360

When quenching in still and agitated liquids, well known dimensionless similarity equations can be used to calculate HTCs (Kraus, *et al.*, 2001, Lienhard, *et al.*, 2005).

What does mean an exponent from the point of view of physics?

An exponent means that thermal equilibrium establishes when time is infinity and process with different initial temperatures to simultaneously approaches the equilibrium. To see that physically, assume that there are two barrels: 200 liters and 100 liters in volume (see Fig. 4). The volume of cups every single second decreases according to exponential law $V = V_0 \exp(-m^{\ddagger})$ and it is calculated as $\Delta V_I = 200L[\exp(-0.1\ddagger_i) - \exp(-0.1\ddagger_{i+1})]$; $\Delta V_{II} = 100L[\exp(-0.1\ddagger_i) - \exp(-0.1\ddagger_{i+1})]$. The result of calculations are presented in Table 4. The exponential process means that the first barrel every single second loses twice more water as compared with the second one (see Fig. 4). The volume of cups every single second decreases according to exponential law $V = V_0 \exp(-m^{\ddagger})$ and it is calculated as $\Delta V_I = 200L[\exp(-0.1\ddagger_i) - \exp(-0.1\ddagger_{i+1})]$; $\Delta V_{II} = 100L[\exp(-0.1\ddagger_{i+1})]$. The result of exponential law $V = V_0 \exp(-m^{\ddagger})$ and it is calculated as $\Delta V_I = 200L[\exp(-0.1\ddagger_i) - \exp(-0.1\ddagger_{i+1})]$. The result of calculated as $\Delta V_I = 200L[\exp(-0.1\ddagger_i) - \exp(-0.1\ddagger_{i+1})]$. The result of exponential law $V = V_0 \exp(-m^{\ddagger})$ and it is calculated as $\Delta V_I = 200L[\exp(-0.1\ddagger_i) - \exp(-0.1\ddagger_{i+1})]$. The result of calculated as $\Delta V_I = 200L[\exp(-0.1\ddagger_i) - \exp(-0.1\ddagger_{i+1})]$. The result of calculated as $\Delta V_I = 200L[\exp(-0.1\ddagger_i) - \exp(-0.1\ddagger_{i+1})]$. The result of calculated as $\Delta V_I = 200L[\exp(-0.1\ddagger_i) - \exp(-0.1\ddagger_{i+1})]$. The result of calculated as $\Delta V_I = 200L[\exp(-0.1\ddagger_i) - \exp(-0.1\ddagger_{i+1})]$. The result of calculations are presented in Table 4. The same story will take place in the next second. At the end of exponential process in the first barrel will be two molecular of water and in the second barrel will be only one molecular of water.



Fig, 4. An example with two volumes of liquid and two cups to explain meaning of exponential law of cooling: according to exponential law, volume a) every single second loses two time more water as compared with volume b)

Table 4. Changing of volumes of cups vs. time according to exponential law: index I is cup a) and index II is cup b)

‡, <i>s</i>	1	2	3	4	5	Ν	$\ddagger \rightarrow \infty$
$\Delta V_I, L$	19	17	16	14	13		2 molecular
$\Delta V_{II}, L$	9.5	8.5	8	7	6.5		1 molecular

The first micro-cup will take two molecular of water and the second one will take one molecular of water. At this point, the process is finished simultaneously since there is no more water in both barrels. In fact, the considered process is a final value. The same is observed when cooling steel parts from different initial temperatures. The thermal equilibrium is established in finite period of time due to existence of temperature fluctuations (see Fig. 5)..

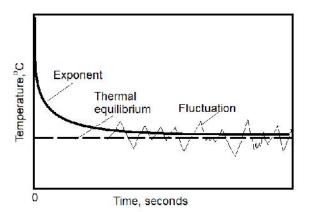


Fig. 5. Fluctuations destroying exponential law of cooling when temperature difference approaches the amplitude of fluctuation

According to Levich (Levich, 1962) the temperature fluctuations depend on the absolute temperature T and can be approximately calculated as

$$\Delta T \approx 10^{-10} T \tag{15}$$

At null temperature the value $\Delta T \approx 10^{-10} \times 273^{\circ} K \approx 2.73 \times 10^{-8}$. Taking this fact into account, one can calculate Eeq for different initial temperatures 200°C and 100°C. They are:

It means that thermal equilibrium for the first experiment establishes in 354 seconds and for the second experiment in 347 seconds and both are not infinity but rather small numbers:

For both experiments thermal equilibrium is established approximately in 350 seconds. Difference between them is $\pm 0.86\%$. Such detail consideration is needed to understand how one should image the thermal equilibrium establishment in the practice. For

practical use, one can consider thermal equilibrium when dimensionless temperature # in Eq. (8) decreases, for example, in 1000 times. Then it means that difference between core temperature and coolant will be 0.2 oC in first experiment and 0.1 oC in the second experiment. It is almost the same and will take three times less time as compared with the time created by fluctuations.

Experimental validations

To check correctness of generalized Eq. (13), the spherical sample 60 mm in diameter was manufactured from the metallic material thermal properties of which are presented in Table 5. In the center of ball a semi-conductor was instrumented providing ideal contact with the tested material and sensitive of measurement less than 0.1%.. A special scheme of measurement was used to provide high sensitive of temperature measurement. The sample was heated in thermostat to 1000C; 80oC; 60oC; 50oC; 30oC; and 20oC and then cooled in agitated ice water at 0oC. Convective heat transfer coefficients for agitated ice water are provided in Table 5. The cooling time in all experiments was within 127 - 130 seconds (see experimental data in Table 5). As one can see from Table 5, instead of big difference (more than 3 times) in initial temperature, the cooling time depicted by very sensitive semiconductor, was almost the same, 128 seconds in average.

Table 5. Thermal diffusivity (a) and thermal conductivity (b) of metal tested probe vs. temperature

Temperature °C	Thermal diffusivity, $a \times 10^6 [m^2 s^{-1}]$	Thermal conductivity, [Wm-1K-1]
20	22	77
24	21.7	76
30	21.45	75.5
40	21.2	75
60	20	73
80	19.5	71.4
100	18.5	71.5

Table 6. Transition time from 1000 C, 80°C... and 30°C to temperature 0°C when cooling metal spherical probe of 60 mm diameter in agitated ice water at 0°C (initial temperature was changed about 1000 times)

Initial tempe rapture of probe	Average HTC, W/m2K	Transition time, s Experiment
100	2900	127
80	2870	128
60	2700	130
50	2614	130
30	2440	129

According to Eq. (13) and Table 2, the average cooling time of spherical metallic probes is:

$$\ddagger_c = E_{eq} \frac{K}{aKn} = 7.28 \times \frac{91.1 \times 10^{-6} m^2}{20 \times 10^{-6} m^2 / s \times 0.26} \approx 127 \text{ sec}$$

that coincides very well with the experimental data presented in Table 6.

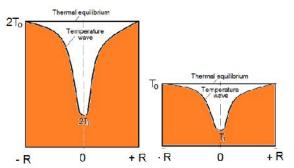


Fig. 6. A scheme of the temperature penetration in cylindrical sample when Biot number tends to infinity: a) surface temperature mentais at 2T0 and b) surface temperature mentais at T0

DISCUSSION

Why one should consider the time of thermal equilibrium establishment? The processes of cooling and heating are complicated because steel parts are complicated such as gears with many teeth. Metallurgical engineers use one minute per one mm of thickness. For example, soak time for cylindrical specimen of 30 mm in diameter is 30 minutes. In many cases heating time is 1.5 - 2 times longer as it should be in reality. Using proposed generalized equation, one can save energy, time by decreasing heating time in furnaces, making simplified calculations. Also, it can be an express method for quick calculations of thermal equilibrium establishment since general equations in this case contains only three parameters: a, K and Kn. More information on heat transfer processes one can find in the well known books (Bergles, 1998, Kraus *et al.*, 2001; Lienhard IV and Lienhard V, 2016). More precise data it possible to generate when solving hyperbolic heat conductivity equation with the appropriate boundary condition. Especially, solving of hyperbolic heat conductivity is needed when big temperature gradients take place as shown in Fig. 6 and more information can be obtained to understand what is thermal equilibrium and how it is established (Buiks, 2009, Bobinska *et al.*, 2010 and Buike *et al.*, 2015).

Conclusion

According to classical heat conductivity theory, the thermal equilibrium tends to be established when time is infinity and doesn't depend significantly on initial temperature. It is proposed to consider thermal equilibrium establishment when dimensionless $r_{m} = \frac{T_0 - T_m}{T_m}$

temperature $\int_{-\infty}^{\infty} \frac{1}{T-T_m} decreases 1000$ times. Based on this approach, a very simple correlation is proposed for engineers to help

them easily and quickly calculate heating (cooling) time of any object in condition of $0 \le Bi_V \le \infty$. According to simplified correlation, the duration of the thermal equilibrium establishment is directly proportional to Kondratjev form factor K, inversely proportional to thermal diffusivity of a material and Kondratjev number Kn and depends on the accuracy of the temperature measurement. Generalized equation can be used in many industrial branches: in heat treating industry, food production industry, in cryogenic processing and other industrial activities. There is no contradiction between main postulate (zeroth law) of thermodynamics and exponential law of heating (cooling) if temperature fluctuations are taken into account which result in dissipation of thermal energy and thermal equilibrium establishment. More accurate analysis on thermal equilibrium establishment can be performed by analyzing analytical solutions of hyperbolic heat conductivity equation with the appropriate boundary and initial conditions.

List of Symbols

T is temperature;[‡] is time; An are temperature amplitudes; Un are eigenfunctions dependent on coordinates; k = 1; 2; 3 for plate like form, cylindrical form and spherical form; K is Kondratjev form coefficient in m2; a is thermal diffusivity of

material or liquid in m2/s; λ is thermal conductivity of material in W/mK; R is radius in m; D is diameter in m; α_{conv} is heat

transfer coefficient (HTC) in W/m2K; T_m is bath temperature; V is emittance; S is surface in m2; V is volume in m3; BiV is generalized Biot number; Kn is Kondratjev number; Eeq is indicator showing how much times initial temperature difference is decreased.

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