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Thermogravimetry and the Negative Temperature Dependence of Gravity

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Abstract

It is shown that data of thermogravimetric measurements confirm the negative temperature dependence of gravity. The accounting of this dependence is necessary for increase of accuracy of the thermogravimetric analysis. Physical prerequisites of the phenomenon are briefly considered. Possible influence of the observed effect of weight reduction by a form of the electric arc discharge is noted.

Keywords: temperature, gravitation, thermogravimetric analysis, mass, plasma

1. Introduction

The thermogravimetric analysis based on exact weighing of the heated sample is widely applied in researches of physical and chemical properties of materials (Wendlandt, 1974; Simons, Newkirk, & Aliferis, 1957; Sestak, 1984). The first stage of thermogravimetric measurements is receiving a basic curve – temperature dependence of weight of the empty holder of a sample, for example, of a crucible. At data processing of temperature measurements the basic curve is subtracted from experimental temperature dependence of weight. Out of areas of change of phase structure of substance in which there are sharp changes of its weight, the main reason for the monotonous increasing temperature dependence of weight is considered action of forces of buoyancy. Meanwhile, physical temperature dependence of weight of bodies (Dmitriev, Nikushchenko, & Snegov, 2003; Dmitriev, 2007; Dmitriev, 2008; Dmitriev, 2012a; Dmitriev & Bulgakova, 2013) has essential impact on measurements of weight and has to be taken into account in the exact thermogravimetric analysis; this circumstance was noted by Grumazesku (2015).

2. Temperature dependence of Gravity Force

Negative temperature dependence of physical weight of bodies – the experimental fact confirmed by a set of measurements. The majority of these measurements were taken in a normal laboratory conditions, thus influence of artifacts – buoyancy (buoyancy force of pushing out in the atmosphere), temperature change of the sizes of a sample, thermal air convection, action of electric and magnetic fields were carefully considered. Various types of high-precision scales, various designs of the weighed containers, various materials of samples and various methods of their heating were used (ultrasound, a heat transfer from the electric heater and a chemical way) (Dmitriev, 2007; Dmitriev, 2008; Dmitriev, 2012a). One of the recent experiments showing negative temperature dependence of weight is described in (Dmitriev & Bulgakova, 2013).

2.1 Experiment

The design of container, in which heating of a tight steel cylinder made of stainless steel was carried out by a chemical method, is shown in Figure 1.

Diameter of the external brass-cylinder is 60 *mm*, height - 62 *mm*, thickness of walls - 3.5 *mm*, weight - 475 *g*; diameter of the internal cylinder - 45 *mm*, height - 46 *mm*, thickness of walls - 4.5 *mm*, weight - 280 *g*. In the condition specified in the figure the temperature of the internal cylinder is constant, the weight of completely equipped container is equal to 773.7651*g*.

Measurements of weight with a margin error readout of 0.1 *mg* were also carried out with laboratory scale of XP2004S mark at temperature of air in a working room equal to 19.8 °C, humidity - 31.8 %, pressure - 1022 *hPa*.

In the course of measurements the container was overturned, then the current value of its weight was registered. In the overturned condition, inside the small cylinder, there is going a process of partial dissolution of crystals NaOH (masse of 5 *mg*) in distilled water (masse of 6 *mg*) which is accompanied by heat release. The temperature of the mix in the first seconds of reaction grows by 10 °C, and, as have been shown by special measurements, the average temperature of the internal temperature of the mix in the first seconds of reaction grows by 10 °C, and, as have been shown by special measurements, the average temperature of the internal cylinder, owing to a heat transfer, is smoothly increased by 3-4 °C within the first two-three minutes. A specific feature of the given experiment is that, first, the process of dissolution of crystals of alkali is not accompanied by release of gases and, due to reliable sealing of covers of containers, the release of air from small and big cylinders (and the corresponding handicap to weighing) is absent. Second, due to the big weight of the external cylinder, the temperature of its surface, owing to a heat transfer, increases during the first two minutes by no more than by 0.2 °C. As a result, apparent reduction of weight of the container caused by air convection, which is determined by differences of temperatures of the surface of the container and the ambient air, in the first 2-3 minutes of measurements does not exceed 0.1 *mg*. High durability of the external cylinder also practically excludes influence of its weak temperature deformations on change of buoyancy of the weighed container.

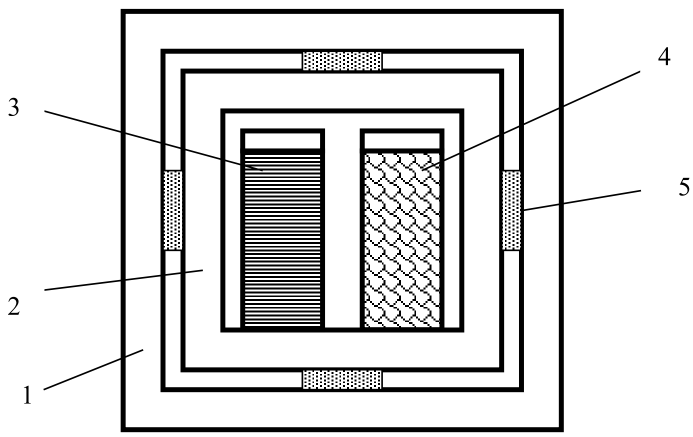

Figure 1. The design of container with chemical heating of the internal cylinder. 1 - the external cylinder; 2 - the internal cylinder; 3 - an open vessel with distilled water; 4 - an open vessel with crystals of NaOH; 5 - polyfoam

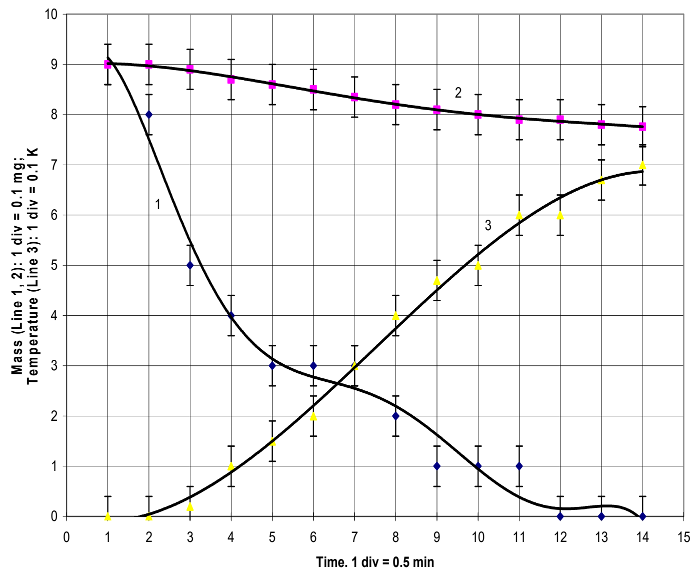

Figure 2. 1 - experimental time dependence of change of weight of container in the overturned position; 2 - calculated dependence of change of weight of the container with account for influence of temperature air convection; 3 - experimental dependence of temperature of the surface of the external cylinder

Figure 2 shows experimental time dependences of weight of container, temperatures of its surface, and the calculated value of weight caused by temperature convection of air close to the walls of the container. Obviously, the paths of curves 1 and 2 essentially differ, accompanied by a typical sharp fall of weight of the container during the first minutes of measurements.

Let's estimate influence of temperature artefacts on the results of measurements of weights of samples. Change Δm_1 of apparent weight of the container, caused by change of volume of the steel cylinder owing to thermal expansion of its material is equal to

$$\Delta m_1 = \frac{3\pi}{4}\rho d^2 h\alpha\Delta T \quad , \tag{1}$$

where ρ - density of air, α - factor of linear expansion of material of the cylinder, d - its diameter, h - height. Change Δm_2 of apparent weight of the container, caused by deformations of walls of the cylindrical vessel, owing to temperature change of air pressure ΔP within its volume, as it is possible to show on the basis of the theory of elasticity (Dmitriev & Bulgakova, 2013), is equal to:

$$\Delta m_2 = \frac{\pi\rho h d^3\Delta P}{4\delta E} + \frac{\pi\rho d^3}{16}\sqrt[3]{\frac{3(1-\nu)d\Delta P}{2\delta E}} \tag{2}$$

where δ - thickness of walls, E - the modulus of elasticity and ν - Poisson's ratio . The size ΔP is connected to change of temperature ΔT of air within the volume of the external cylinder $\Delta P = P\Delta T / T$, where P - normal pressure of atmosphere and T - temperature of air in the cylinder. The given estimate is overestimated, as in the second addend of formula 2, describing deformation of face walls of a vessel, such walls are presented by thin membranes; actually, the deflection of end faces is less than it is supposed in conclusion 2.

The change Δm_3 of apparent weight of the container, caused by air convection due to difference ΔT of temperatures of surface of the external steel cylinder and temperatures of air in the closed box of analytical balance, will be estimated on the basis of Gläser (1990) according to which

$$\frac{\Delta m_3}{A d^{1/4}\Delta T^{3/4}} = 9.2\cdot 10^{-7}\, g cm^{-9/4} K^{-3/4} \tag{3}$$

where the area of lateral surface of the cylinder is $A = \pi d h$.

In Table 1 the experimental and calculated values of change of weight of container, corresponding to the third minute of measurements are given. In the given calculations the density of air $\rho = 1.19 kg/m^3$, $\Delta T = 3^0 K$ (obviously overestimated value), $\Delta P = 1020 N/m^2$.

Table 1. Calculated Total ($\Delta m_\Sigma = \Delta m_1 + \Delta m_2 + \Delta m_3$) and experimental ($\Delta m$) temperature reduction of weight of container

d, mm	h, mm	δ, mm	$\alpha\cdot 10^6$, K^{-1}	ν	$E\cdot 10^{-10}$, N/m^2	ΔT, K	Δm_1, mcg	Δm_2, mcg	Δm_3, mcg	Δm_Σ, mcg	Δm, mcg
60	62	3.5	18.9	0.36	9	0.22	2.6	$\prec 290$	54	$\prec 346$	640

Obviously, observable (registered) reduction of weights of containers essentially, with account for errors of measurements, exceeds calculated one.

2.2 Simple Phenomenological Model

Proceeding from the principle of inertness of mechanical system, that is, its tendency to preserve the stable state, accelerated under action of external, for example, elastic force of movement of a test body downwards should cause an increment $\Delta\vec{g}_p$ of acceleration of the gravity applied to a body which is directed from the centre of the Earth. On the contrary, the accelerated movement of a trial body upwards is accompanied by increase of acceleration of the gravity applied to a body by value $\Delta\vec{g}_c$. Values $\Delta\vec{g}_p$ and $\Delta\vec{g}_c$, generally speaking, can be different. Change of acceleration of the gravity acting on a body, moving with acceleration $\vec{a}$ under influence of the elastic force, in the elementary (linear) approximation, is represented as

$$\Delta\vec{g}_{p,c} = -\frac{\vec{g}_0}{|\vec{g}_0|}(\vec{g}_0\cdot\vec{a})A_{p,c} \quad , \tag{4}$$

where symbols p,c mean passing (p) and a contrary (c), in relation to a direction of vector $\vec{g}_0$ of normal acceleration of a gravity, orientation of a vertical projection of vector $\vec{a}$ of acceleration of external forces, and factors A_p and A_c characterize a degree of change of values $\Delta\vec{g}_{p,c}$. If the body under action of the external, electromagnetic in nature, elastic force makes harmonious oscillations along a vertical with frequency ω and amplitude b , the average for the period $\tau = 2\pi / \omega$ of fluctuations value $\Delta\overline{g}$ of change of acceleration of free falling (AFF) of such mechanical oscillator is equal to the sum of average changes of AFF in movement of a body passing and contrary to vector $\vec{g}_0$,

$$\Delta\overline{g} = \Delta\overline{g}_p + \Delta\overline{g}_c \quad , \tag{5}$$

and at constant $g_0 = |\vec{g}_0|$ it is equal

$$\Delta\overline{g} = -\frac{g_0 b\omega^2}{\pi}(A_p - A_c) \quad . \tag{6}$$

From 6, it follows that at $A_p \succ A_c$, the average acceleration of free falling of mechanical oscillator, for example, a rotor with a horizontal axis of rotation, is less than value g_0 of normal acceleration of the gravity force. The reduction, averaged on several series of the measurements of the apparent weight of a rotor with horizontal axis, was observed in experiment (Dmitriev & Bulgakova, 2013), by results of which for the material of a rotor (stainless steel) it is possible to approximately estimate the order of value of difference $(A_p - A_c) \approx 10^{-7} g_0^{-1}$.

The absolute values of factors A_p and A_c can be measured on the basis of the shock mechanical experiments accompanied by the high, above $10^5 ms^{-2}$ accelerations of interacting bodies. For steel samples the order of values A_p and A_c is approximately equal to $10^{-2} g_0^{-1}$.

If to consider as the mentioned above trial body a microparticle of a solid body bound together by forces of interatomic interaction with other similar particles, formulas 1-3 allow to explain influence of temperature on acceleration of free falling (weight) of such body (Dmitriev, Nikushchenko, & Snegov, 2003). Thermal movement of microparticles of a solid body is accompanied by their significant accelerations, in so doing, the average value a_s of a projection of these accelerations on a vertical is proportional to average speed of chaotic movement of microparticles. In a classical approximation, at a body temperature higher than the one of Debye-temperatures, the acceleration a_s is in direct ratio to a square root from an absolute body temperature T ,

$$a_s = C\sqrt{T} \quad , \tag{7}$$

where C - the factor dependent on physical properties of a material.

In one-dimensional approximation, we can consider a test body as a chain of microparticles bound by elastic forces, as shown in Dmitriev, Nikushchenko, and Snegov (2003), Dmitriev and Bulgakova (2013),

$$C \propto \frac{v}{\sqrt{\mu}} \quad , \tag{8}$$

where v - speed of a longitudinal acoustic wave in a solid test body and μ - its density.

Formally, having replaced in equation (6) the average for the period of fluctuations magnitude of acceleration $b\omega^2 / \pi$ with average acceleration of particles a_s , we shall present the temperature dependence $P(T)$ of weight of a body as

$$P(T) = P_0(1 - B\sqrt{T}) \quad , \tag{9}$$

where m - weight of a body, $P_0 = mg_0$, $B = C(A_p - A_c)$.

In a small range of temperatures the linear dependence of changes ΔP of weight and ΔT of a body temperature is satisfied,

$$\Delta P = -P_0 B \frac{\Delta T}{2\sqrt{T}} \quad . \tag{10}$$

Negative temperature dependence of weight of not-magnetic metal samples at close to normal ($300K$) temperatures of bodies experimentally proves to be true, in so doing, the relative change of weight for a unit of temperature

$$\gamma = \frac{\Delta P}{P_0 \Delta T} = -\frac{B}{2\sqrt{T}} \quad , \tag{11}$$

is equal to several units $10^{-6}K^{-1}$ (Dmitriev, Nikushchenko, & Snegov, 2003; Dmitriev & Bulgakova, 2013).

The typical increase of value γ along with reduction of density of a sample material is observed that is in agreement with (8) (Dmitriev, Nikushchenko, & Snegov, 2003) (we should note that outside the limits of considered classical approximation, for example, at close to zero absolute temperatures of bodies, formulas 7-8 are not satisfied).

3. Thermogravimety

At creation of a basic curve the seeming mass M of the holder (crucible) in air is equal $M = m - \rho V$, where m - the mass of a crucible, V - its volume and ρ - air density. Temperature change of the seeming weight

$$\frac{dM}{dt} = \frac{dm}{dt} - \rho\frac{dV}{dt} - V\frac{d\rho}{dt} \quad , \tag{12}$$

where $V = V_0(1+\beta t)$, β - volume expansion coefficient of material of a crucible.

Temperature dependence of $\rho(t)$ is represented by known expression

$$\rho(t) = \frac{A}{1+Bt}\cdot\frac{p}{760} \quad , \tag{13}$$

where $A = 0.0012932 g/cm^3$, $B = 0.00367K^{-1}$, p - air pressure in mm Hg (Ebert, 1957).

By normal ($p = 760$) air pressure Eq. 12 my be represent as

$$\rho(t) = \frac{A}{1+Bt}\cdot\frac{p}{760} \quad , \tag{14}$$

where $C_1 = -V_0\beta A(1+Bt)^{-1}$ and $C_2 = V_0(1+\beta t)AB$.

For numerical estimates we will use results of work Simons, Newkirk, and Aliferis (1957) according to which the seeming change of mass of a porcelain crucible with the weight $m = 4g$ and volume $1.5cm^3$ measured on Shevenar's thermoscales in the temperatures range $200-1000^0C$ is equal $4.0\cdot10^{-6}gK^{-1}$.

Volume coefficient of expansion of porcelain $\beta = 9\cdot10^{-6}K^{-1}$ (Ebert, 1957) and, for example, at $t = 200^0C$, the values of coefficients $C_{1,2}$ are equal $C_1 = -1.0\cdot10^{-8}gK^{-1}$ and $C_2 = 7.1\cdot10^{-6}gK^{-1}$. As the absolute values $C_1 \prec\prec C_2$, the main contribution to the seeming change of mass of a crucible is made by the effects of buoyancy described by coefficient C_2. Obviously, the consent of the experimental and provided settlement data is possible only at $\frac{dm}{dt} = -3.1\cdot10^{-6}gK^{-1}$. This fact directly confirms the negative temperature dependence of weight of bodies. Temperature change of weight of the holder, it is generally connected with change of temperature of a porcelain crucible, the assessment of size of relative temperature change of the weight of porcelain from where follows the $\gamma = \frac{dm}{mdt} \approx -0.8\cdot10^{-6}K^{-1}$. Sign and an order of the specified size correspond to data of measurements of physical temperature dependence of weight of various metals (Dmitriev, Nikushchenko, & Snegov, 2003; Dmitriev, 2007; Dmitriev, 2008), and also PZT-ceramic (Dmitriev, 2012b).

4. About Possible "Pushing Out" of Plasma by a Gravitational Field

As appears from 8, 9, the greatest loss of weight as a result of its physical negative temperature dependence is reached in materials with a small density μ, a high speed of a sound v and at high absolute temperatures. It is interesting to note that it follows from formula 9 that at very high temperatures T exceeding value of $B^{-1/2}$, the weight value P of a sample changes a sign, i.e. such sample has to be pushed out by a gravitational field. Today the highest temperatures are achievable in nuclear reactions, and also in plasma of an arc electric discharge. For example, in the typical arc discharge in the air, temperature of plasma reaches 12 000 K (Raizer Yu, 1991; Lafferty & Cobine, 1980). The shape of the arc discharge is defined by action of an electric and magnetic fields, and also forces of convection and buoyancy (Archimedes).

Nevertheless, in certain experimental conditions, for example, in vacuum, in the absence of Archimedes force, gravitation forces, including, the effects of loss of weight described by formula 9, have to influence a shape of the arc discharge considerably. It is remarkable that though the shape of the electric arc discovered by the Russian scientist Petrov in 1802 is explained by action of forces of buoyancy, the electric discharge in “vacuum” (at very low pressure) also often has a shape of the arc with its top up.

Special research has to show whether the characteristic shape of an electric arc in vacuum confirms the phenomenon of temperature dependence of weight. This result is also interesting for interpretation of dynamics of nuclear explosions in the atmosphere.

5. Conclusion

For more exact quantitative estimates of influence of temperature dependence of weight on results of thermogravimetric measurements, the accounting of the sizes, forms, masses, physical and thermodynamic characteristics as holder, and the studied sample is necessary. Temperature dependence of physical weight of bodies will allow to establish the reasons of anomalies of thermogravimetric dependences with bigger degree of reliability and to increase the accuracy of the gravimetric analysis.

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