

## THE ISSUE OF CALCULATING THE FINAL TEMPERATURE OF THE PRODUCTS OF RAPID EXOTHERMIC CHEMICAL REACTIONS WITH SIGNIFICANT ENERGY RELEASE IN A CLOSED VOLUME

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The theoretical problem solved in this article is the calculation of thermodynamic parameters such as final temperature, distribution of the liquid and dry saturated vapour phases of the substance that are considered to be in thermodynamic equilibrium, and pressure of the system of several reaction products after adding to the system a certain amount of heat or the thermal effect released during rapid exothermic reaction in a closed volume that occurs so fast that it can be considered to be adiabatic, and when the volume of liquid reagents is several orders of magnitude less than the volume of the reactor. The general multi-substance problem is reduced to a theoretical problem for one substance of calculation thermodynamic parameters of system after adding a certain amount of heat that gives theoretically rigorous isochoric calculation. In this article, we substantiate our view that isochoric pass of calculation is more robust compared to seemingly more natural isobaric pass of calculation, if the later involves quite not trivial calculation of the adiabatic compression of a two-phase system (liquid – **dry** saturated vapour) that can pass itself into another kind of state (liquid – **wet** saturated vapour), which requires, apparently, more complex descriptions compared with isochoric calculation because the specific heat capacity of wet saturated vapour can be negative.

The solved theoretical problem relates to a practical problem that has been a driver for our research as part of a design of the reactor of the titanium reduction from magnesium and titanium tetrachloride supplied into atmosphere of the reactor at high temperatures when both reagents are in gaseous state. The reaction is known to be exothermic with a high thermal effect, and estimate of the final temperature and pressure of the products of reaction, for instance, designing the reactor allows eliminating the possibility of the reaction products to penetrate backwards into supply tracts of the reagents. Using a rigid theoretical approach and heuristics of thermodynamic parameters of reaction products available in the literature, we have presented a graphical dependence of final temperature, pressure ratio of the liquid and vapour state of titanium after the reaction on the initial temperature of the reactor and magnesium in the range of 1200–1800 °K while titanium tetrachloride is injected into reactor at its critical temperature.

**Keywords:** *final temperature of the reaction products, isochoric calculation, rapid exothermic chemical reaction*

## 1. INTRODUCTION

Thermal effect  $\Delta H_{298}$  of exothermic chemical reactions [1] taking place in hermetically closed reactor volumes may be so large that the reaction products are in the gaseous state at very high pressures and temperatures. In such cases and especially when the initial temperature of the reactants is high, one of the important problems during designing of chemical reactors is estimating thermodynamic characteristics of the reaction products in the final state of the reaction process. If the reaction proceeds rapidly enough then the adiabatic condition can be applied to the theoretical calculation as a good approximation of the thermodynamic characteristics of the process, and they frequently are close enough to the maximum temperatures of the reaction observed experimentally.

In general, to determine the theoretical temperature of the reaction the heat balance of the process is made [2] as follows: the value of the total amount of heat -  $\Delta H_{298}$  together with the sum of the enthalpies of the reactants is obtained for a temperature at which they enter the reaction, then after the reaction the product is heated by this heat from 298°K to the desired temperature considering also the heat of polymorphic transformations, melting and evaporation of reaction products, etc., the process equation is developed and then it is solved with respect to the reaction temperature.

It is not difficult to calculate the heating process and the final temperature of the reaction products assuming that the heating process is isobaric. This corresponds to the situation when the volume of the reactor must be increased in the course of the reaction to maintain the pressure at the baseline level. The volume during the theoretical isobaric calculation has been increased. It is necessary to establish a further adiabatic compression of the reaction products to the original volume. However, during this theoretical compression process of the reaction products, generally speaking, various phase transitions must be passed, including compression of dry saturated vapour and then compression of wet saturated vapour, which is a two-phase system where dry saturated vapour coexists in thermodynamic equilibrium with the liquid and at further compression condenses into a liquid phase, and so on. The complexity of the last part of calculation path described above depreciates relative ease of the part of isobaric calculation. Therefore, generally speaking, if possible such a pass of calculation should be avoided unless there is a substantial reasoning to do otherwise, and we regard that direct isochoric calculation may be a safer and easier approach, especially if the reaction is fast and the adiabatic condition can be regarded as a good approximation. It should be noted that the heating process in the solid phase, including melting, complies with the isochoric condition and can be taken from the isobaric calculation. It should also be noted that the heating of the reaction products in the form of wet vapour – a two-phase system, where dry saturated vapour coexists in thermodynamic equilibrium with the liquid phase in a constant closed volume – is the most problematic part of the calculation. The peculiarity of the processes in two-phase systems (isochoric heating, quantitative ratio of the phases at the end of the reaction, adiabatic compression and others) is related ultimately to the fact that the specific heat capacity of dry saturated vapour of any substance, in general, is negative [4], [5]. As the distance from the critical point increases, specific heat remains negative but its absolute value decreases, then it becomes zero and during further

increase becomes positive. In these conditions, negative specific heat means that heating (rising of the temperature) of saturated vapour causes it to release a certain amount of heat. The isochoric evaporation of liquid is a kind of process that in our opinion should be best described in a general way on the basis of the theory developed in [3]. It should be noted that the adiabatic compression of a two-phase system (liquid – **dry** saturated vapour) can pass itself into another kind of state (liquid – **wet** saturated vapour) [3], which requires, apparently, more complex descriptions compared with isochoric heating.

Next, we present a thermodynamic calculation of the adiabatic heating of a two-phase system consisting of dry saturated vapour coexisting in thermodynamic equilibrium with the liquid phase, enclosed in a volume of constant size, when a certain amount of heat is added to the system.

The theoretical calculation will be further applied in order to get assessment of the final temperature of the reaction  $TiCl_4 + 2Mg \rightarrow 2MgCl_2 + Ti$  in a closed volume of a reactor of constant certain size and temperature that happens there, assuming that both ingredients are in a gas-vapour phase of the same temperature as the body of the reactor.

## 2. PROBLEM STATEMENT

Two phases – liquid and its dry saturated vapour – of a homogeneous substance are situated in a closed volume of constant size in a thermodynamic equilibrium at temperature  $T_1$ , where  $m'$  is the mass of the liquid,  $m''$  is the mass of the dry saturated vapour, and  $m' + m'' = m = const$ .

We consider that the two-phase system is isolated, and a certain amount of heat  $Q$  is added to it so that the system performs a transition from one thermodynamic equilibrium state of phases at the temperature  $T_1$  to a new thermodynamic equilibrium state of phases at the temperature  $T_2$  to be found. Our task is to calculate  $T_2$  as well as a quantity ratio of the masses of both phases of the system at the end of the process. Considering our reaction proceeds rapidly, we neglect interaction with the walls, so the process is considered to be adiabatic. Temperature range is limited from below by melting temperature  $T_m$  of liquid, and from the top by temperature  $T_{ev}$  in which all the liquid mass  $m'$  in volume  $V$  would evaporate and all the substance would become dry saturated vapour. In order to comply with the above condition, value of  $Q$  should not exceed the one that is necessary to evaporate the entire mass  $m'$  of the liquid.

It is important to note that the thermodynamic equilibrium phase transition at volume  $V = const$  means that the isochoric process applies to the system as a whole so that the liquid phase process is on the left of the boundary curve, while the saturated vapour process is on the curve at the right boundary, i.e. the vapour at all times remains only dry saturated vapour [1].

## 3. NOTATIONS

$T$  – the absolute temperature.

$P_v(T)$  – the pressure of dry saturated vapour at temperature  $T$  (i.e., all the vapour is under thermodynamic equilibrium with the liquid; it is not superheated vapour, and

no saturated liquid or wetness is present in the atmosphere, and therefore all the liquid if any exists only in the bottom of volume of the considered system).

$Q$  – the quantity of heat.

$V; v$  – the volume and specific volume of the system.

$U; u$  – the internal energy and specific internal energy of the system.

$I; i$  – the enthalpy and specific enthalpy of the system.

$r(T)$  – the specific heat of vaporisation

Once primed quantities refer to the liquid phase, and doubly primed quantities belong to the vapour phase.

$c'; c''$  – the specific heat capacity (liquid and gas) phases of the system.

$V'; V''; v'; v''$  – the volume and specific volume of the substance in the system in respective phases at given temperature  $T$  of the system.

$U'; U''; u'; u''$  – the internal energy of the substance of the system in the respective phases and the specific internal energy phases of the system at given temperature  $T$  of the system.

$I'; I''; i'; i''$  – the enthalpy and specific enthalpy of the system in the respective phases at given temperature  $T$  of the system.

Given the above notation, we can write:

$$V = m \cdot v = V' + V'' = m \cdot (v' + v'')$$

$$U = m \cdot u = U' + U'' = m \cdot (u' + u'')$$

$$I = m \cdot i = I' + I'' = m \cdot (i' + i'').$$

#### 4. THEORY

It should be noted that all the components of the equation of thermodynamic state of the system are functions of temperature  $T$  of the system, which has both liquid and vapour that are in the thermodynamic equilibrium. As described in the previous section, we avoid dealing with the so-called wet vapour and, therefore, consider that the entire mass of the system consists either of liquid or dry saturated vapour. Therefore, we consider that at any temperature  $T$  of the system the equation holds:  $m = m' + m''$ .

Since the process is isochoric, all the heat added to the system increases the internal energy of the system:

$$dQ = dU = dU' + dU'' \quad (1)$$

Adding to the system some heat  $dQ$ , part of the mass of the liquid phase converts into vapour, and the distribution of energy is obtained as follows:

$$dU' = d(m' \cdot u') = m' \cdot du' + u' \cdot dm' \quad (2)$$

$$dU'' = d(m'' \cdot u'') = m'' \cdot du'' + u'' \cdot dm'' \quad (3)$$

Here, we assume that each next state after adding additional heat  $dQ$  is also in thermodynamic equilibrium and contains either dry vapour or liquid, and the atmosphere in the volume of the system does not contain wet vapour. Therefore, the equation holds  $m' = m - m''$  and  $dm' = -dm''$ .

Since  $i = u + P \cdot v$  and process is isochoric  $di = du + P \cdot dv + v \cdot dP$ ,  $di = du + v \cdot dP$ . Given that the change in temperature of the system is possible only by changing the mass distribution of the system between the liquid and vapour phase, with increasing temperature some part of the liquid will evaporate and conversely. Therefore, when calculating the specific enthalpy of the system it is required to take into account the specific heat of evaporation  $r(T)$  required for the phase transition. We have:  $i'' = i' + r$ ,  $u' = i' - P_v \cdot v'$  and  $u'' = i'' - P_v \cdot v''$ .

$$\begin{aligned} u'' &= (i' + r) - P_v \cdot v'' + (P_v \cdot v' - P_v \cdot v') = (i' - P_v \cdot v') + r + \\ &+ P_v \cdot (v' - v'') \text{ and we get:} \\ u'' &= u' + r + P_v \cdot (v' - v'') \end{aligned} \quad (4)$$

Thus, the overall relationship between the specific internal energy of system  $u'$  and  $u''$  is given by equations (6–54) and (6–61) from [3].

$$\int_{T_0}^T dU' = u'(T) - u'(T_0) = \int_{T_0}^T c'_p \cdot dt - \int_{T_0}^T P_v \cdot \frac{dv'}{dt} \cdot dt \quad (5)$$

$$c'_p(T) = c_p(T) - T \cdot \left( \frac{\partial v'}{\partial T} \right)_p \cdot \frac{dP_v}{dT} \quad (6)$$

where  $c_p(T)$  – specific isobaric heat capacity of the liquid phase,

$u'_0 = u'(T_0)$  – specific internal energy at certain temperature  $T_0$ .

Substituting (2) and (3), (4) (1) we obtain the following transformations:

$$dQ = dU = dU' + dU'' = m \cdot du' + d\{[r + P_v \cdot (v' - v'')] \cdot m''\} \quad (7)$$

Integrating (7) from temperature  $T_1$  of the initial state to temperature  $T_2$  of the final state of the system, we find heat  $Q$  that has been added to the system:

$$\begin{aligned} Q &= U(T_2) - U(T_1) = m \cdot \int_{T_1}^{T_2} c'_p \cdot dt - m \cdot \int_{T_1}^{T_2} P_v \cdot \frac{dv'}{dt} \cdot dt + \\ &+ r_{liq}(T_2) \cdot m''(T_2) - r_{liq}(T_1) \cdot m''(T_1) + \\ &+ P_v(T_2) \cdot [v'(T_2) - v''(T_2)] \cdot m''(T_2) - \\ &- P_v(T_1) \cdot [v'(T_1) - v''(T_1)] \cdot m''(T_1) \end{aligned} \quad (8)$$

Equation (8) together with (6) gives the solution to the problem statement in a general form, and gives the equation of state of vapour to calculate  $m''(T_1)$  and  $m''(T_2)$ , as well as gives formulas for the calculation of:  $P_v = P_v(T)$  saturated vapour pressure;

$c_p = c_p(T)$  specific isobaric heat capacity of the liquid phase;

$r_{liq} = r_{liq}(T)$  specific heat of vaporisation of liquid  
density of the liquid phase depending on temperature  $\rho_{liq} = \rho_{liq}(T)$ , and assessment of  $\left(\frac{dv'}{dt}\right)_p$  and  $\frac{dv'}{dt}$ .

Taking into account

$$P_v(T_2) \cdot [v'(T_2) - v''(T_2)] \cdot m''(T_2) = -P_v(T_2) \cdot \left[ V - V'(T_2) - \frac{m''(T_2)}{\rho_{liq}(T_2)} \right] \quad (9a)$$

$$P_v(T_1) \cdot [v'(T_1) - v''(T_1)] \cdot m''(T_1) = -P_v(T_1) \cdot \left[ V - V'(T_1) - \frac{m''(T_1)}{\rho_{liq}(T_1)} \right] \quad (9b)$$

$$\left(\frac{\partial v'}{\partial t}\right)_p = \beta(T) \cdot v'(T) = \frac{\beta(T)}{\rho_{liq}(T)} \quad (9c)$$

where  $\beta(T)$  is the coefficient of the volumetric thermal expansion, as well as integrating by parts the second integral in (5)

$$\int_{T_1}^{T_2} P_v \cdot \frac{dv'}{dt} dt = \frac{P_v(T_2)}{\rho_{liq}(T_2)} - \frac{P_v(T_1)}{\rho_{liq}(T_1)} - \int_{T_1}^{T_2} v'(t) \cdot \frac{dP_v}{dt} dt \quad (9d)$$

we obtain (8) in its final form:

$$\begin{aligned} Q = U(T_2) - U(T_1) = & m \int_{T_1}^{T_2} c_p(t) dt + m \cdot \int_{T_1}^{T_2} v'(t) \cdot [1 - \beta(t) \cdot t] \cdot \frac{dP_v}{dt} dt - \\ & - m \cdot \left[ \frac{P_v(T_2)}{\rho_{liq}(T_2)} - \frac{P_v(T_1)}{\rho_{liq}(T_1)} \right] + r_{liq}(T_2) \cdot m''(T_2) - r_{liq}(T_1) \cdot m'(T_1) - \\ & - P_v(T_2) \cdot \left[ v - v'(T_2) - \frac{m''(T_2)}{\rho_{liq}(T_2)} \right] + P_v(T_1) \cdot \left[ v - v'(T_1) - \frac{m''(T_1)}{\rho_{liq}(T_1)} \right] \end{aligned} \quad (10)$$

## 5. CALCULATION OF THE AMOUNT OF HEAT Q FOR EVAPORATION OF LIQUID IN GIVEN VOLUME V AND TEMPERATURE $T_{ev}$

For a given mass of substance with molecular weight  $\mu$  in the volume  $V = const$  there is a temperature, which we will call **the temperature of complete evaporation** and denote by  $T_{ev}$ , in which all the mass  $m$  in volume  $V$  will evaporate becoming dry saturated vapour. This temperature can be estimated from the system of van der Waals equation with constants  $a$ ;  $b$  appropriate to the substance, and the formula for vapour pressure ( $P_v$ )

$$\text{where } \left[ P + \left( \frac{m}{\mu} \right)^2 \cdot \frac{a}{V^2} \right] \cdot \left( V - \frac{m}{\mu} \cdot b \right) = \frac{m}{\mu} \cdot R \cdot T_{ev} \text{ where } P = P_v(T_{ev}) \quad (11)$$

solved with respect to temperature  $T_{ev}$ . However, more accurately  $T_{ev}$  can be

determined if we know the temperature dependence of the density of dry saturated vapour  $\rho_v = \rho_v(T)$ . Obviously,  $m = V \cdot \rho_v(T_{ev})$ . Sources [6]–[9] propose and use a formula, which compared to the experiment gives the mean square error in the range of 2 %–4 %:

$$\rho_v(T) = \frac{\mu P_v(T)}{RT} \cdot \frac{1}{Z_c + (1 - Z_c) \cdot (1 - x)^y}, \text{ where } Z_c = \frac{P_c \cdot v_c}{R \cdot R_c}, x = T_{red}^{0.7}, y = 0.33 \cdot T_{red}^{0.7}, \quad (12)$$

$$\text{reduced temperature } T_{red} = \frac{T}{T_c}$$

where  $P_c$  [MPa];  $V_c$  [cc/mole];  $T_c$  [° K] are critical parameters,  $\rho_v(T)$  [g/cc];  $R = 8.314$  [J/(mol·K)], and  $\mu$  [g/mol] is molecular weight.

Value  $Q$  is obtained from (8) or (10) considering that  $T_1$  is the initial temperature of liquid,  $T_2 = T_{ev}$ ,  $V'(T_{ev}) = 0$ ,  $m''(T_2) = m$ . ( $m'(T_1)$  can be evaluated from (11) at  $T = T_1$ ,  $m = m'$  and solving it with respect to  $m'$ . Temperature dependence  $\rho_{liq}(T)$  should be taken from the literature, for example, [6], [10], [11] or to estimate approximately from [8], [9].

In the continuous methods of production of titanium [12], this occurs when calculating evaporation of magnesium and titanium tetrachloride. When evaluating  $Q$  to completely evaporate liquid, it is required to put  $T_1 = T_m$ . But most of all, as noted in the introduction, the importance of a theoretically rigorous calculation of  $Q$  is preferred to estimate the temperature and pressure of gases and vapours, and phase ratio of the products of exothermic reaction, which is developed in the course of the reaction at high initial temperatures of the reagents. In this regard, the following reaction is typical



and it occurs in the gas-vapour phase with a sufficiently high initial temperature of reagents, and with significantly high standard thermal effect  $\Delta H_{298} = 62.5$  [kcal/(g·mol)].

Below are presented the final results of calculation of temperature of reaction (13), the partial pressures of the reaction products of magnesium chloride  $MgCl_2$  and titanium  $Ti$ , as well as calculation of the ratio of liquid and vapour phases of titanium depending on the initial temperature of the isothermal body of reactor, which is also the temperature of the reagent magnesium of the reaction.  $V = 30$  litres is the volume of the reactor. Before the start of the reaction, this volume contains the amount of magnesium that evaporates completely creating dry saturated vapour of magnesium at the given initial temperature of the reactor. Then gaseous titanium tetrachloride  $TiCl_4$  in a stoichiometric ratio with magnesium is injected into the reactor always at the same temperature of 638 °K, which is its critical temperature.

The reaction product of magnesium dichloride  $MgCl_2$  will always be in the vapour or gaseous state, but titanium  $Ti$  will be in a two-phase thermodynamic equilibrium state of liquid and dry saturated vapour. Due to the very rapid reaction with extensive evolution of heat, the heat transfer to the reactor walls during reaction can be neglected and considered that it starts only upon completion of the reaction.



Therefore, the interaction with the walls of the reactor is not considered in the calculation process, and the reaction is considered to be adiabatic.

We have done also calculations for various volumes of the reactor. Our calculations show extremely weak dependence of the final reaction temperature on the reactor volume for the same initial temperature, and the corresponding amount of the reagent Mg as described above – the amount that creates dry saturated vapour of Mg without the liquid phase, and  $\text{TiCl}_4$  in stoichiometric proportion. Hence, the partial pressure of  $\text{MgCl}_2$  and the pressure of saturated vapour Ti will be almost the same, which is confirmed by calculation.

The range of initial temperatures of the body of reactor covered by the calculation is 1200 °K–1800 °K, with the step of 5 °K. Equation (10) obtained in the previous section binds the temperature and other thermodynamic parameters of one substance with adding of a certain amount of heat. However, in our case the products of our reaction (13) consist of two substances that share the same volume. It should be noted that total volume of the reaction products in liquid form is by three orders of magnitude smaller than the reactor, and therefore we can neglect it. On the other hand, considering reaction products in the vapour and gas state – they can normally co-exist and share the same volume so that the total pressure is a sum of the partial pressures of each substance. Therefore, calculation of the final temperature and other thermodynamic parameters for each substance using equation (10) can be done independently disregarding that they share the same volume, assuming that the volume of reactor is sufficiently big as in our case.

For each given increment of temperature, we can calculate independently for each substance the heat required for the said temperature increase, and can calculate the sum of the calculated heat. For the given standard thermal effect of the given exothermic chemical reaction, we can calculate the final temperature and other thermodynamic parameters of the products of reaction.

## 6. RESULTS

The results of calculations are presented in Figs. 1–3.

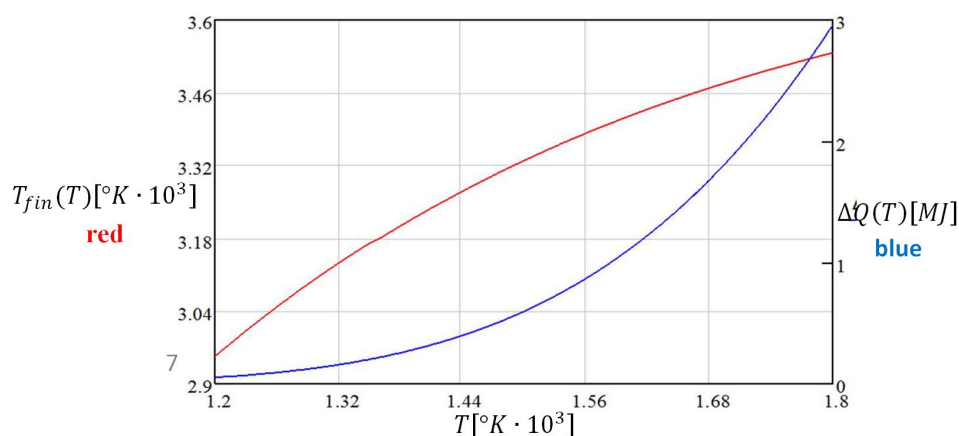


Fig. 1. Dependence of the final temperature and heat on the initial temperature of the reactor and magnesium, and injecting titanium tetrachloride at its critical temperature.



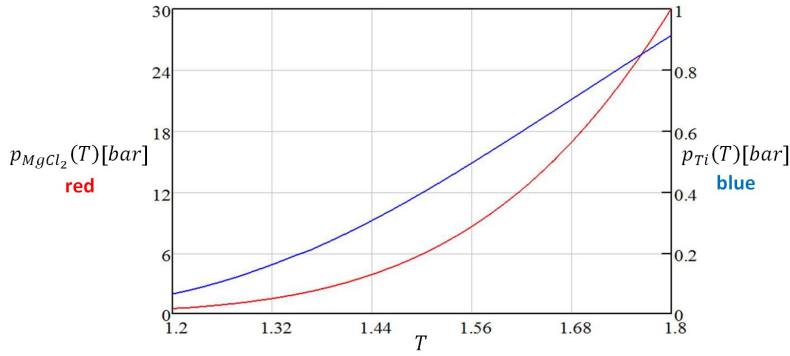


Fig. 2. Dependence of the pressure of the reaction products on the initial temperature of the reactor and magnesium.

In Fig. 1, the horizontal axis is  $T[^\circ K \cdot 10^3]$  where  $T$  is the initial temperature of the body of the reactor where reaction (13) will proceed. It should be noted that reagent Mg initially before the reaction is at the same temperature as the body of the reactor and its mass is exactly so big to create dry saturated vapour in the volume of 30 litres of the reactor. The left vertical axis is  $T_{fin}[^\circ K \cdot 10^3]$  (line is coloured red) where  $T_{fin}$  is the final calculated temperature of the reaction products after reaching thermodynamic equilibrium state of the products after adding to them the standard thermal effect of exothermic reaction (13). The right vertical axis is  $\Delta Q(T)[MJ]$  in mega joules (line is coloured blue) where  $\Delta Q$  is the thermal effect of the reaction.

In Fig. 2, the horizontal axis is  $T[^\circ K \cdot 10^3]$ , the same as in Fig. 1. The left vertical axis is the partial pressure  $p_{MgCl_2}(T)[bar]$  of vapour of reaction product  $MgCl_2$  (graphic is red). The right vertical axis is partial pressure  $p_{Ti}(T)[bar]$  of the dry saturated vapour of reaction product titanium Ti (graphic is blue).

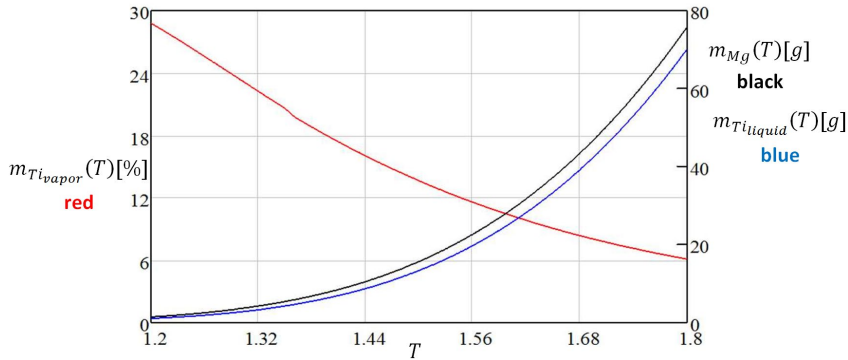


Fig. 3. Dependence of the ratio of the liquid and vapor state of titanium after the reaction on the initial temperature of the reactor and magnesium.

In Fig. 3, the horizontal axis is  $T[^\circ K \cdot 10^3]$ , the same as in Fig. 1. The left vertical axis is the mass of the dry saturated vapour of titanium as a percentage of the total mass of the titanium reduced during reaction (13) (graphic is red). The first right vertical axis is the mass of liquid titanium as percentage of the total mass of titanium reduced during reaction (13) (graphic is black). The second right vertical axis is the mass of liquid titanium as percentage  $m_{Ti\_vapor}(T)[\%]$  of the total mass of titanium reduced during reaction (13) (graphic is blue).

## 7. CONCLUSIONS

We have derived expression (10) that binds the temperature increase and other changes in other thermodynamic parameters of the system with a certain amount of heat that has to be added to the system in order to get the said changes. Then we have applied this equation to a situation with two substances that share the same volume, and we can do this way so far as the volume of reactor is significantly bigger than the volume of reagents and/or products of reaction in the liquid phase. Then after using pretty extensive numeric calculations, we have obtained the dependencies in graphical form for a case of the reactor volume of 30 litres and temperature range of 1200–1800 °K and presented them graphically in Figs. 1–3.

It should be noted that Fig. 3 demonstrates at first view a strange result that increasing temperature of the reactor, the vaporous part of the titanium decreases. Actually, it is the case due to our condition that titanium tetrachloride should always be injected at the same critical temperature of 638 °K.

Considering the practically achievable temperature range of the reactor body of the gaseous reaction of titanium reduction to be between 1450–1650 °K, we can estimate that at the temperature of the reactor body at 1650 °K at the end of the reaction temperature of the reaction products for even a short moment should not exceed 3600 °K and pressure should not exceed 16 bar. In order to keep the pressure at any moment in the reactor below 10 bar, the temperature of the reactor should not exceed 1500 °K.

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## PAR GALA PRODUKTU TEMPERATŪRAS APRĒĶINA JAUTĀJUMU SLĒGTĀ APJOMĀ STRAUJI NOTIEKOŠAI EKSOTERMISKAI ĶĪMISKAI REAKCIJAI AR IEVĒROJAMU ENERĢIJAS IZDALĪŠANOS

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### K o p s a v i l k u m s

Vairāku vielu sistēmas jeb reakcijas produktu termodinamisko parametru aprēķina problēma tiek reducēta uz teorētiski stingru izohorisku termodinamisko parametru aprēķinu vienai vielai pēc zināma siltuma daudzuma pievienošanas sistēmai. Šajā rakstā mēs pamatojam viedokli, ka termodinamisko parametru izohoriskā aprēķina paņēmieni ir uzticamāks par šķietami dabisko izobārisko aprēķina veidu, jo izobāriskajā aprēķinā ir jāietver adiabatiskas saspiešanas aprēķins divfāžu sistēmas netriviālajā gadījumā, kad šķidruma – sausā piesātinātā tvaika sistēma var pāriet citā sistēmā, kurā ir termodinamisks līdzsvars starp šķidrumu un slapju piesātinātu tvaiku, kurš acīmredzot prasa ievērojami sarežģītākus aprēķinus salīdzinot ar izohorisko aprēķinu, jo vispārīgā gadījumā piesātinātā tvaika īpatnējā siltumietilpība var būt negatīva.

Motivācija atrisināt šo teorētisko problēmu bija saistīta ar praktisku uzdevumu - reaktora projektēšanu, kurā augstā temperatūrā gāzveida reaģentu magnija un titāna tetrahlorīda reakcijas rezultātā tiek reducēts titāns. Šī reakcija ir pazīstama kā izteikti eksotermiska ar augstu siltuma efektu. Reakcijas gala temperatūras, spiediena un šķidrās un gāzveida fāzes reakcijas produktu sadalījuma aprēķini reaktora projektēšanas procesā ir ļoti svarīgi, piemēram, lai neļautu reakcijas produktiem iespieties reaģentu padošanas kanālos. Pielietojot stingru teorētisku aprēķinu un izmantojot zinātniski-tehniskajā literatūrā pieejamās reakcijas produktu termodinamisko parametru vērtību heuristiskās funkcijas atkarībā no temperatūras, raksta otrajā daļā mēs uzrādām aprēķinu rezultātā iegūtās grafiskās diagrammas reakcijas beigu temperatūrai, reakcijas produktu spiedienam un šķidrās vielas un tvaika sadalījumam atkarībā no reaktora un magnija sākuma temperatūras 1200–1800°K diapazonā, kamēr titāna tetrahlorīdu vienmēr reaktorā ievada vienā un tajā pašā gāzes kritiskajā temperatūrā.

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