General Decreasing Solutions to the Equation Arises in Cryochemistry

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1 Introduction

We investigate properties of a solution to the ordinary differential equation arises in mathematical models describing the physico-chemical processes occurring during a cryochemical modification of drug substances (see [6, 7]).

Under these assumptions, the thermal conductivity equation with mass transfer for the one–dimensional case can be used to calculate the temperature field created by the carrier gas stream:

$$\frac{\partial T}{\partial t} = V\,\frac{\partial T}{\partial x} - \frac{\mu}{\rho C_V}\cdot\frac{\partial}{\partial x}\Big(\lambda\,\frac{\partial T}{\partial x}\Big). \tag{1.1}$$

Here ρ, μ, λ are the density (kg/m^3), molecular weight (kg/mol), thermal conductivity $(\mathrm{W}/(\mathrm{m}\cdot\mathrm{K}))$ of the carrier gas, respectively, C_V is the molar heat capacity of the carrier gas at constant volume $(\mathrm{J}/(\mathrm{mol}\cdot\mathrm{K}))$, V is the linear velocity of the carrier-gas flow front (m/s).

In stationary mode we have $\partial T/\partial t = 0$ and equation (1.1) reduces to the ordinary differential equation

$$\frac{dT}{dx} - \frac{\mu}{\rho V C_V}\cdot\frac{d}{dx}\Big(\lambda\,\frac{dT}{dx}\Big) = 0. \tag{1.2}$$

The flow rate of the carrier gas is controlled during the experiment with the help of an external device (an industrial gas pipeline with accuracy, according to its passport data, not worse than 5%). The regulated gas stream of the carrier, passing through a heated copper screen (a mixed molecular flow shaper) of cylindrical shape, heats up to a certain temperature, captures the vapors of the initial substance and takes them out into the vacuum space. Let the nozzle area of the mixed molecular flow shaper be $S(\mathrm{m}^2)$. Then the molar flow rate of the carrier gas is dN/dt(mol/s) and can be written as

$$\dot N = \frac{dN}{dt} = \frac{\rho V S}{\mu}\,.$$

In this case, the ratio of the molar flow rate of the carrier gas dN/dt (mol/s) to the nozzle area of the mixed molecular flow shaper, that is, the density of the carrier gas flow dn/dt $(\mathrm{mol}/(\mathrm{m}^2\cdot\mathrm{s}))$ can be represented as

$$\dot n = \frac{dn}{dt} = \frac{\dot N}{S} = \frac{\rho V}{\mu}\,.$$

Therefore, equation (1.2) can be written as

$$\frac{dT}{dx} - \frac{d}{dx}\left(\frac{\lambda}{C_V\dot{n}} \cdot \frac{dT}{dx}\right) = 0.$$

It can be solved analytically, taking into account the dependence of the thermal conductivity of the carrier gas on the temperature. An interesting fact is that the heat capacity of gases in a wide range of pressures practically does not depend on the pressure. This circumstance received its explanation from the molecular kinetic theory. A large number of gases, such as nitrogen, helium, argon, carbon dioxide, etc., have the square-root dependence of the thermal conductivity on the temperature expressed by the approximate formula

$$\lambda = \frac{ik}{3\pi^{3/2}d^2}\sqrt{\frac{RT}{\mu}}\,, \tag{1.3}$$

where

- i is the sum of translational and rotational degrees of freedom of molecules (5 for diatomic gases, 3 for monatomic ones),
- k is the Boltzmann constant,
- μ is the molar mass,
- T is the absolute temperature,
- d is the effective diameter of molecules,
- R is the universal gas constant.

Representing λ in (1.3) as $\alpha\sqrt{T}$ with the appropriate coefficient α, we obtain

$$\frac{\lambda}{C_V\dot{n}} = \frac{\alpha\sqrt{T}}{C_V\dot{n}} = b\sqrt{T} \ \text{ with } \ b = \frac{\alpha}{C_V\dot{n}}\,.$$

Now the thermal conductivity equation with mass transfer of these process for the one–dimensional case can be transformed to the ordinary differential equation [5]:

$$\frac{d}{dx}\left(T - b\sqrt{T}\,\frac{dT}{dx}\right) = 0, \ \ b > 0. \tag{1.4}$$

We study the dependence of the temperature on the distance under three types of boundary conditions, namely the Dirichlet, Neumann, and Robin ones.

The Dirichlet condition specifies the temperature value at the boundary.

The Neumann condition specifies the boundary value for the derivative of the temperature.

In the Robin condition, we specify a linear combination of the temperature value and the derivative of the temperature at the boundary.

The coefficient of the temperature value in the Robin condition is the Biot number (the ratio of the conductive thermal resistance inside the object to the convective resistance at the surface of the object).

The mathematical model was discussed with colleagues from the Department of Chemistry of M. V. Lomonosov Moscow State University T. A. Shabatina, and Yu. Morozov.

2 General decreasing solutions

Theorem 2.1. *Each positive solution T to equation* (1.4) *is either constant or strictly monotonic. Each strictly decreasing solution has the form*

$$T(x) = c^2\,\Theta\Big(\frac{x-x^*}{bc}\Big)^2, \tag{2.1}$$

where x^* and $c>0$ are arbitrary constants, while Θ is a decreasing function $(-\infty;0)\to(0;1)$ implicitly defined by

$$x = 2\Theta(x) + \ln\frac{1-\Theta(x)}{1+\Theta(x)}\,. \tag{2.2}$$

The left-hand side of (1.4) *contains an expression in parentheses which must be constant and, for the solution defined by* (2.1)*, equals c^2.*

If maximally extended, such T is defined on the interval $(-\infty;x^*)$ and satisfies

$$T(x)\to c^2 \ \text{ and } \ T'(x)\to 0 \ \text{ as } \ x\to-\infty, \tag{2.3}$$

$$T(x)\to 0 \ \text{ and } \ T'(x)\to -\infty \ \text{ as } \ x\to x^*. \tag{2.4}$$

Proof. First, by the substitution $T=Z^2$ with $Z>0$ we convert equation (1.4) into the form

$$(Z^2-2bZ^2Z')'=0,$$

which immediately yields

$$Z^2-2bZ^2\,Z'=C=const$$

with further transformations depending on $\operatorname{sgn} C$.

If $C=0$, then either $Z\equiv 0$ or $1=2b\,Z'$, which entails that $Z'>0$ and Z is strictly increasing.

If $C=-c^2<0$, then we obtain $Z^2+c^2=2bZ^2Z'$. This shows again that $Z'>0$.

Finally, if $C=c^2>0$ with $c>0$, then we obtain

$$Z^2-c^2=2bZ^2Z'. \tag{2.5}$$

Now, if $Z(x)=c$ at some point x, then, by the uniqueness theorem, Z must coincide with the constant solution $Z\equiv c$. If not, then either $Z>c$ on the whole domain or $Z<c$. We reject the first case (with $Z'>0$ due to (2.5)) as well as the previous constant one.

In the second case we put

$$Z(x)=c\,z\Big(\frac{x}{bc}\Big),\quad 0<z<1,$$

which converts (2.5) into

$$z^2-1=2z^2z'. \tag{2.6}$$

This can be written as

$$1=\frac{2z^2z'}{z^2-1}=\Big(2+\frac{2}{z^2-1}\Big)z',$$

whence, for $0<z<1$,

$$x-a=\int\limits_0^{z(x)}\Big(2+\frac{2}{\zeta^2-1}\Big)\,d\zeta = 2z(x)+\ln\frac{1-z(x)}{1+z(x)}$$

with some a. We have a general family of implicitly defined strictly decreasing solutions to (2.6) satisfying $0<z<1$. One of them, with $a=0$, is just Θ defined by (2.2). All others can be obtained from Θ by a horizontal shift. Thus, we have (2.1).

It follows from (2.2) that

$$\begin{aligned}\Theta(x) &\to 0 \ \text{ as } \ x \to 0,\\ \Theta(x) &\to 1 \ \text{ as } \ x \to -\infty.\end{aligned}$$

Then, using (2.6), we obtain

$$\begin{aligned}\Theta'(x) &\to -\infty \ \text{ as } \ x \to 0,\\ \Theta'(x) &\to 0 \ \text{ as } \ x \to -\infty.\end{aligned}$$

These limits, together with (2.1), produce the first three limits in (2.3) and (2.4). For the fourth one, we use (2.5) to obtain

$$T' = 2ZZ' = \frac{Z^2 - c^2}{2bZ} = \frac{T - c^2}{2b\sqrt{T}} \to -\infty \ \text{ as } \ T \to 0. \quad \square$$

3 On existence and uniqueness of solutions

Theorem 3.1. *For any constants $x_0 < x_1$ and $T_1 > T_0 > 0$, equation* (1.4) *has a unique solution T defined on $[x_0; x_1]$ and satisfying the conditions*

$$T(x_0) = T_0, \quad T(x_1) = T_1. \tag{3.1}$$

Proof. The boundary conditions show that, according to Theorem 2.1, the solution T must strictly decrease and therefore have the form given by (2.1) and (2.2). So, the boundary conditions become

$$\frac{\sqrt{T_j}}{c} = \Theta\Big(\frac{x_j - x^*}{bc}\Big), \ \ j \in \{0, 1\},$$

or, by using (2.2),

$$\frac{x_j - x^*}{bc} = 2\frac{\sqrt{T_j}}{c} + \ln\frac{1 - \frac{\sqrt{T_j}}{c}}{1 + \frac{\sqrt{T_j}}{c}}\,, \ \ j \in \{0, 1\}. \tag{3.2}$$

Thus, we have to prove the existence and uniqueness of a pair (x^*, c) satisfying (3.2). Putting

$$q := \sqrt{\frac{T_1}{T_0}} \in (0; 1) \ \text{ and } \ k := \frac{\sqrt{T_0}}{c} \in (0; 1), \tag{3.3}$$

we write the difference of the two equations (3.2) as

$$\frac{k(x_1 - x_0)}{b\sqrt{T_0}} = 2k(q - 1) + \ln\frac{(1 - qk)(1 + k)}{(1 + qk)(1 - k)}$$

or

$$\frac{x_1 - x_0}{2b\sqrt{T_0}} = F_q(k) \tag{3.4}$$

with

$$F_q(k) := f(k) - qf(qk), \tag{3.5}$$

$$f(k) := \frac{1}{2k}\,\ln\frac{1 + k}{1 - k} - 1. \tag{3.6}$$

Lemma 3.1. *For each $A > 0$ and $q \in (0;1)$, there exists a unique $k \in (0;1)$ such that $F_q(k) = A$ with F_q defined by* (3.5) *and* (3.6)*. The mapping $(A,q) \mapsto k$ is a C^1 function $(0;+\infty)\times(0;1) \to (0;1)$ strictly increasing with respect to both A and q.*

Proof. Note that

$$f(k) = \frac{\ln(1+k)}{2k} - \frac{\ln(1-k)}{2k} - 1,$$

whence $f(k) \to 0$ as $k \to 0$ (by L'Hôpital's rule) and $f(k) \to +\infty$ as $k \to 1$.

Now we study the derivative of f by using its Taylor series uniformly converging on any subsegment of the interval $(0,1)$.

$$\begin{aligned} f'(k) &= \frac{1}{2k(1+k)} - \frac{\ln(1+k)}{2k^2} + \frac{1}{2k(1-k)} + \frac{\ln(1-k)}{2k^2} = \frac{1}{k(1-k^2)} - \frac{\ln(1+k)}{2k^2} + \frac{\ln(1-k)}{2k^2} \\ &= \frac{1}{k}\sum_{n=0}^{\infty} k^{2n} + \frac{1}{2k^2}\sum_{n=1}^{\infty}\frac{((-1)^n-1)k^n}{n} = \frac{1}{k}\sum_{n=0}^{\infty} k^{2n} - \frac{1}{k^2}\sum_{m=0}^{\infty}\frac{k^{2m+1}}{2m+1} \\ &= \frac{1}{k}\sum_{n=0}^{\infty}\Big(1-\frac{1}{2n+1}\Big)k^{2n} = \frac{1}{k}\sum_{n=1}^{\infty}\frac{2n}{2n+1}k^{2n} = \sum_{n=1}^{\infty}\frac{2n}{2n+1}k^{2n-1} > 0, \end{aligned}$$

whence $f(k) > 0$ as well.

Further,

$$f''(k) = \sum_{n=1}^{\infty}\frac{2n(2n-1)}{2n+1}\,k^{2n-2} > 0,$$

whence f' is strictly increasing and

$$\frac{dF_q}{dk}(k) = f'(k) - q^2 f'(qk) > 0.$$

So, F_q is strictly increasing in k, $F_q(k) \to 0$ as $k \to 0$, and

$$F_q(k) = (1-q)f(k) + q(f(k) - f(qk)) > (1-q)f(k) \to +\infty \ \text{ as } \ k \to 1.$$

Therefore, F_q must attain, exactly once, each $A > 0$, which proves the first part of Lemma 3.1.

The second part follows immediately from the implicit function theorem and the evident inequalities

$$\begin{aligned} \frac{\partial(F_q(k)-A)}{\partial A} &= -1 < 0, \\ \frac{\partial(F_q(k)-A)}{\partial q} &= -f(qk) - qkf'(qk) < 0. \end{aligned}$$ □

We return to proving Theorem 3.1. Having the unique value of k satisfying (3.4), we obtain, from (3.2) and (3.3), the unique values

$$c = \frac{\sqrt{T_0}}{k} > \sqrt{T_0} \ \text{ and } \ x^* = x_1 - 2b\sqrt{T_1} - bc\,\ln\frac{c-\sqrt{T_1}}{c+\sqrt{T_1}}$$

to satisfy (3.2). This completes the proof of Theorem 3.1. □

Now we will to prove two theorems concerning other boundary conditions for equation (1.4).

Theorem 3.2. *For any real constants $x_0 < x_1$, $T_0 > 0$, and $U_1 < 0$, equation* (1.4) *has a unique solution T defined on $[x_0; x_1]$ and satisfying the conditions*

$$T(x_0) = T_0, \quad T'(x_1) = U_1.$$

Theorem 3.3. *For any real constants $x_0 < x_1$, $T_0 > 0$, and $U_1 < 0$, equation* (1.4) *has a unique solution T defined on $[x_0; x_1]$ and satisfying the conditions*

$$T(x_0) = T_0, \quad T'(x_1) = U_1 T(x_1).$$

Proof. We try to prove the existence and uniqueness of a constant $T_1 \in (0; T_0)$ such that the unique solution T existing according to Theorem 3.1 satisfies the boundary conditions of the related theorem.

According to Theorem 2.1, $T - b\sqrt{T}\,T' = c^2$, whence, using notation (3.3),

$$T'(x_1) = \frac{T(x_1) - c^2}{b\sqrt{T(x_1)}} = \frac{q^2 T_0 - T_0/k^2}{bq\sqrt{T_0}} = \frac{k^2q^2 - 1}{k^2 q} \cdot \frac{\sqrt{T_0}}{b}\,,$$
$$\frac{T'(x_1)}{T(x_1)} = \frac{k^2q^2 - 1}{k^2q^3} \cdot \frac{1}{b\sqrt{T_0}}\,,$$

where $k \in (0; 1)$ is chosen, depending on $q \in (0; 1)$, to provide the boundary conditions (3.1) for the solution T defined by (2.1).

It follows from Lemma 3.1 that $k \in (0; 1)$ strictly increases with respect to $q \in (0; 1)$. So, in both right-hand sides of the last equations, the numerator $k^2q^2 - 1$ is negative and strictly increases in q, while its absolute value decreases. The denominators are positive and also strictly increase. Thus, the fractions are negative with strictly decreasing absolute values.

Now consider their limits at 0 and 1.

Both fractions tend to $-\infty$ as $q \to 0$. As for $q \to 1$, there must exist $k_1 = \lim\limits_{q\to 1} k \in (0; 1]$.

If $k_1 < 1$, then it follows from (3.4)–(3.6) that

$$0 < \frac{x_1 - x_0}{2b\sqrt{T_0}} = F_1(k_1) = f(k_1) - 1 \cdot f(1 \cdot k_1) = 0.$$

This contradiction shows that $k_1 = 1$. (For this k_1, no contradiction arises because $f(k) \to +\infty$ as $k \to 1$.) Hence

$$T'(x_1) \to 0 \ \text{ and } \ \frac{T'(x_1)}{T(x_1)} \to 0 \ \text{ as } \ q \to 1.$$

So, both expressions strictly increase from $-\infty$ to 0 as q increases from 0 to 1 (i.e. as T_1 increases from 0 to T_0). Therefore, they both must attain, exactly once, each negative value, and this proves Theorems 3.2 and 3.3. □

Remark 3.1. The authors' results connected with mathematical modeling in other physical processes can be found in [1–4].

Acknowledgements

The reported study was partially supported by RSF, Project # 20-11-20272 and MSU Program of Development, Project # 23-SCH05-26.

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