ON THE EXPRESSIONS OF THE TYPE $\oint dF = 0$ AND THE STATE AND PATH FUNCTIONS IN CHEMICAL THERMODYNAMICS

I. Mathematical formalism and the true significance of line integrals in chemical thermodynamics – internal energy and work

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Mathematical aspects of the state and path function concepts are discussed. It is shown by rigorous mathematical analysis, appealing on the definition of line integrals of the second type, that the widespread usage of notations of the type $\int d'_{\text{м}}$, in the case of hydrostatic systems, is mathematically incorrect and a new symbol for the total work (physical quantity that is not a state function of a system) in such cases is proposed. Green's formula is applied on a typical thermodynamic problem as a proof of the independence of the value of the line integral of the second type over linear differential form on the path of integration if the linear differential form is a total differential of a state function.

Key words: line integrals; linear differential forms; state functions; path functions; thermodynamic systems; thermodynamic cycles; internal energy; work

INTRODUCTION

The main criterion for a given physical quantity to appertain to the set of state functions of systems[1], as is well known, is the independence of its change (due to the change of the system's state) on the path of the process along which the change is being made [1]. Mathematically formulated, the previous attitude goes:

The physical quantity F_1 is a state function of a given system if the line integral along the closed contour of the form:

$$\oint dF_1$$

is identically equal to zero, i.e.:

$$\oint dF_1 = 0 \qquad (1)$$

The previous equation implies that the value of the line integral is independent on the contour of integration (arbitrary line segment), but depends only on the choice of the initial and final points (that represent initial and final state of the system, respectively). The

convenience of such mathematical formalism for representation of physical quantities that are not functions of the path of the processes, but depend only on the state of the system, is obvious.

From a mathematical viewpoint, the previous equation is satisfied if dF_1 is true differential (full, exact, or total differential of a function) [2]. Let us suppose that F_1 is a state function, that can be represented as a function of two independent intensive parameters with which the state of a system is uniquely defined, i.e.:

$$F_1 = F_1(x_1, x_2) \qquad (2)$$

In such case, the total differential of this function is given by:

$$dF_1 = P_1(x_1, x_2)dx_1 + P_2(x_1, x_2)dx_2 \qquad (3)$$

where

$$P_1(x_1, x_2) = \frac{\partial F_1(x_1, x_2)}{\partial x_1} \qquad (4)$$

and

$$P_2(x_1, x_2) = \frac{\partial F_1(x_1, x_2)}{\partial x_2} \qquad (5)$$

According to the Euler's theorem [3]:

$$\frac{\partial}{\partial x_2}\left(\frac{\partial F_1(x_1, x_2)}{\partial x_1}\right) = \frac{\partial}{\partial x_1}\left(\frac{\partial F_1(x_1, x_2)}{\partial x_2}\right) \qquad (6)$$

or, in concordance with previously introduced symbols:

$$\frac{\partial P_1(x_1, x_2)}{\partial x_2} = \frac{\partial P_2(x_1, x_2)}{\partial x_1} \qquad (7)$$

According to all that was previously mentioned, in such a case, the following equation is valid:

$$\int_{AL_1B} P_1(x_1, x_2)dx_1 + P_2(x_1, x_2)dx_2 =$$

$$= \int_{AL_2B} P_1(x_1, x_2)dx_1 + P_2(x_1, x_2)dx_2 \qquad (8)$$

where A and B are, respectively, the initial and the final state of the system (or, more correctly, the points in the x_1x_2 plane that represent those states), and L_1 and L_2 are two different line segments of integration. The last equation is, obviously, a mathematical formulation of the independence of the change of the value of physical quantity F_1 when the system passes from a given initial to a given final state, on the way in which this passage is made. From this equation, it follows, using the properties of line integrals of the second type [2], that:

$$\int_{AL_1B} P_1(x_1, x_2)dx_1 + P_2(x_1, x_2)dx_2 -$$

$$- \int_{AL_2B} P_1(x_1, x_2)dx_1 + P_2(x_1, x_2)dx_2 = 0 \qquad (9)$$

or

$$\int_{AL_1B} P_1(x_1, x_2)dx_1 + P_2(x_1, x_2)dx_2 +$$

$$+ \int_{BL_2A} P_1(x_1, x_2)dx_1 + P_2(x_1, x_2)dx_2 = 0 \qquad (10)$$

and finally:

$$\oint P_1(x_1, x_2)dx_1 + P_2(x_1, x_2)dx_2 = 0 \qquad (11)$$

If F_2 is a state function of a given system, which is uniquely determined by more than two independent parameters, i.e.:

$$F_2 = F_2(x_1, x_2, \ldots, x_n) \qquad (12)$$

it's total differential is given by the equation:

$$dF_2 = \sum_i \left(\frac{\partial F_2}{\partial x_i}\right)_{x_j(j \neq i)} dx_i \qquad (13)$$

The condition of independence of the value of the line integral on the path of integration may be written in the form:

$$\oint \sum_i \left(\frac{\partial F_2}{\partial x_i}\right)_{x_j(j \neq i)} dx_i = 0 \qquad (14)$$

Of course, in the first case (the state function F_1), the integration is performed along a plain curve.

RESULTS AND DISCUSSION

The purpose of the work

Although the previously explained mathematical formalism seems both convenient and easy to understand, still it deserves clarification and further explanation. A typical example is mathematical treatment of work, a physical quantity that is not a state function of a system. The total balance of work in the case of hydrostatic systems is often expressed as a line integral [3] (at least the symbol of line integration is used). So, the total balance of work during a thermodynamic cycle that takes place in a hydrostatic system is often expressed using the symbol for a line integral along a closed contour. This is both mathematically and physically incorrect. Appealing on the rigorous mathematical definitions of Riemann and line integrals, it will be shown that in the described cases, there is no need to

appeal on the generalization of Riemann integrals, i.e. the used notation is incorrect, or, at least, it is not precise. Also, Green's formula will be used as a proof for the independence of the value of the line integral of the second type over linear differential form on the path of integration if the linear differential form is a total differential of a state function, applied to a typical thermodynamic problem.

Mathematical treatment

Let F_1 be a function that represents the internal energy U of a hydrostatic system. If the role of independent variables (arguments) have the thermodynamic temperature T and pressure, P, i.e.:

$$U = U(T, P) \qquad (15)$$

the total differential of this function, i.e. the infinitesimal change of it's value due to the infinitesimal change of the values of the parameters with which the state is fully determined is given by the following equation [3]:

$$dU = \left(\frac{\partial U}{\partial T}\right)_T dT + \left(\frac{\partial U}{\partial P}\right)_T dP \qquad (16)$$

The finite change of the value of this physical quantity, due to the change of the system's state from A_1 to B_1, is a solution of the line integral of the form:

$$\int_{A_1LB_1} dU = \int_{A_1LB_1} \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP \qquad (17)$$

Of course, the path of the integration (the line segment in P,T plane that represents the path of the process) is rigorously defined only if it represents a process that satisfies conditions for thermodynamic reversibility [4].

Having in mind that U is a state function of the system, its change as a result of the change of system's state from A_1 to B_1 is independent on the way in which it was carried out (and also, independent of whether the change was carried out as a result of a reversible or irreversible process). So, it's well enough to postulate a reversible path from the state A_1 to the state B_1, represented by a line segment in P,T plane (or, in general case, X_1,X_2 plane)[2] to calculate the change of internal energy due to a process that leads from the state A_1 to the state B_1.

Because $U = U(T,P)$, the following equations are valid:

$$\left(\frac{\partial U(T,P)}{\partial T}\right)_P = f_1(T,P) \qquad (18)$$

$$\left(\frac{\partial U(T,P)}{\partial P}\right)_T = f_2(T,P) \qquad (19)$$

These equations allow one to write the previous line integral in the form:

$$\int_{A_1LB_1} f_1(T,P)dT + f_2(T,P)dP \qquad (20)$$

The line integral (21) is defined as a sum of the limits [2]:

$$\lim_{\substack{\max \Delta T_i \to 0 \\ n \to \infty}} \sum_{i=1}^{n} f_1(T_i, P_i)\Delta T_i \qquad (21)$$

and

$$\lim_{\substack{\max \Delta T_i \to 0 \\ n \to \infty}} \sum_{i=1}^{n} f_2(T_i, P_i)\Delta T_i \qquad (22)$$

which are, in fact, integral sums of the functions f_1 and f_2 on the contour A_1LB_1 along the coordinates T and P, respectively. ΔP_i and ΔT_i are projections of the line segments Δs_i on the P and T axis, respectively, and P_i and T_i are arbitrarily chosen internal points of the intervals ΔP_i and ΔT_i. In fact, it is *general form* of line integral of the second type (along coordinates) [2].

This integral can be solved using standard mathematical methods [5].

Because the contour of integration A_1LB_1 is, in fact, a line segment in the P,T plane, P and T do not change independently, so one can write:

$$\begin{aligned} T &= \varphi_1(P) \\ P &= \varphi_2(T) \end{aligned} \qquad (23)$$

where $\varphi_2 = \varphi_1^{-1}$.

According to all that was previously mentioned:

$$\int_{A_1LB_1} f_1(T,P)dT + f_2(T,P)dP =$$

$$\int_{A_1LB_1} f_1[T, \varphi_2(T)]dT + f_2[\varphi_1(P), P]dP \qquad (24)$$

or

$$\int_{A_1LB_1} f_1(T,P)dT + f_2(T,P)dP =$$

$$\int_{T_1}^{T_2} f_1[T, \varphi_2(T)]dT + \int_{P_1}^{P_2} f_2[\varphi_1(P), P]dP \qquad (25)$$

and the line integral of the second type (along coordinates) along plain contour, is reduced to a sum of two single integrals.

Alternatively, if P and T are given in parametric form:

$$\begin{aligned} P &= z_1(\xi) \\ T &= z_2(\xi) \end{aligned} \qquad (26)$$

one may write:

$$\int_{A_1LB_1} f_1(T,P)dT + f_2(T,P)dP =$$

$$\int_{\xi_1}^{\xi_2} \left\{ f_1[z_2(\xi), z_1(\xi)]\frac{dz_2(\xi)}{d\xi} + f_2[z_2(\xi), z_1(\xi)]\frac{dz_1(\xi)}{d\xi} \right\}d\xi \qquad (27)$$

In this way, the line integral is reduced to a single integral.

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[2] Here X_1 and X_2 are arbitrarily chosen independent parameters with which the state of the system is uniquely defined.

If the initial and the final states coincide, i.e. in the case of a cycle, represented by a closed curve in the P,T plane, Green's formula [2, 5] may be applied, and the following equation that relates the line integral over a closed contour and the double integral over the corresponding area (closed by the contour that represents the process) is obtained:

$$\oint_{+K} f_1(T, P)\mathrm{d}T + f_2(T, P)\mathrm{d}P = \iint_{\sigma} \left(\frac{\partial f_2}{\partial T} - \frac{\partial f_1}{\partial P} \right) \mathrm{d}T\mathrm{d}P \tag{28}$$

(Here K is the closed contour along which the integration is carried out, and σ is the surface closed with this contour).

If the condition:

$$\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial P} \right) = \frac{\partial}{\partial P}\left(\frac{\partial U}{\partial T} \right) \tag{29}$$

is fulfilled, it follows that:

$$\iint_{\sigma} \left[\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial P} \right) - \frac{\partial}{\partial P}\left(\frac{\partial U}{\partial T} \right) \right] \mathrm{d}T\mathrm{d}P = 0 \tag{30}$$

and further:

$$\oint_{+K} f_1(T, P)\mathrm{d}T + f_2(T, P)\mathrm{d}P = 0 \tag{31}$$

(it's obvious that in the last equation the direction of integration can be omitted from the entry).

Green's formula, according to this, enables more illustrative and more general proof for the independence of the value of the line integral over a linear differential form on the path (contour) of integration, if the linear differential form is an exact differential. It also, rigorously shows that the condition (29) is sufficient [2] for the line integral of the previously mentioned type to be identically equal to zero. It can be easily shown that the condition is necessary, too [2].

Linear differential forms of the type:

$$\sum_i Y_i \mathrm{d}X_i \tag{32}$$

are known in the literature as Pfaffian differential forms [4]. The question about their integrabillity (exactness) is of key importance in thermodynamics [3]. If the Pfaffian linear differential form is an exact differential of a function, than the following equation is valid:

$$\oint \sum_i Y_i \mathrm{d}X_i = 0 \tag{33}$$

If the previously mentioned condition is not fulfilled, than:

$$\oint \sum_i Y_i \mathrm{d}X_i \neq 0 \tag{34}$$

That would be the case of a physical quantity that *is not* a function of the state of a system, and also, a mathematical function of several independent parameters of state of the system, that would represent that physical quantity, does not exist. As an example of such function, one may consider this work. In the case of a hydrostatic system, its element is given by the following equation [3, 4]:

$$\mathrm{d}'w = -P\mathrm{d}V \tag{35}$$

In a general case, the following equation is valid:

$$\mathrm{d}'w = -P\mathrm{d}V + \sum_i Y_i \mathrm{d}X_i \tag{36}$$

where Y_i are generalized forces, and $\mathrm{d}X_i$ are generalized displacements. The element of the work is denoted by $\mathrm{d}'w$ because it is not an exact differential, or, as it has already been mentioned, a function of the type $w = f(X_1, X_2,..., X_n)$ that would represent the work does not exist. So, as is well known, one cannot speak of a definite value of work in a state of a system defined with the multitude of parameters of the state $(X_{10}, X_{20}, ...,X_{n0})$. The system does not "posses" work. The linear differential form, in general case of the type:

$$\mathrm{d}'w = -P\mathrm{d}V + \sum_i Y_i \mathrm{d}X_i \tag{37}$$

is not a total (exact) differential.

If one considers a hydrostatic system, its state is uniquely determined with two independent parameters of the state [3]. This means that an arbitrary state function may be regarded as a function of two independent arguments. The element of work, for such system, is given by (35).

Since $P = P(V)$:

$$\mathrm{d}'w = -P(V)\mathrm{d}V \tag{38}$$

The exchanged work, during the process accompanied with the volume change from V_1 to V_2 can be obtained integrating the last equation:

$$\int \mathrm{d}'w = -\int_{V_1}^{V_2} P(V)\mathrm{d}V \tag{39}$$

However, the change of the volume from V_1 to V_2 may be obtained in various ways. Let us choose a certain path of the process, that leads from the initial state (that one in which the volume has the value V_1) to the final (that one in which the volume has the value V_2). If we represent this process by a set of points (that represent the intermediate states along which the system passes and which are equilibrium states or infinitely close to thermodynamic equilibrium) in a P,V ("indicator") diagram, the work can be calculated by solving the

previous integral (knowing the explicit form of $P(V)$). It is a single, Riemann integral, defined as a limit of the Riemann integral sum [6]:

$$\int_{V_1}^{V_2} P(V)dV = \lim_{\substack{max \, \Delta V_i \\ n \to \infty}} \sum_{i=1}^{n} P(V_i)\Delta V_i \qquad (40)$$

It's obvious that here, the integration is carried out along the V axis.

During the process that leads from the state of the system characterized with the value of volume V_2 to the state characterized with the value of volume V_1, but along a different path of the process compared to the previous, the exchanged work can be calculated solving the integral of the type (taking care, of course, for the sign convention, too):

$$\int d'w = -\int_{V_2}^{V_1} P_1(V)dV \qquad (41)$$

The total balance of work during this cycle is a simple difference of those two integrals:

$$w = -\int_{V_1}^{V_2} P(V)dV - \left(-\int_{V_2}^{V_1} P_1(V)dV\right) \qquad (42)$$

Having in mind the geometrical meaning of the definite Riemann integral, the previous difference (its absolute value) is equal to the area of the surface closed by the contour of the cycle. That means, in this case, one deals with the difference of two Riemann integrals, in which the integration is carried out along the V axis. In the literature [3], for the total balance of work during a cycle in hydrostatic system, often the notations:

$$\oint d'w \qquad (43)$$

and

$$\oint PdV \qquad (44)$$

are used.

Such notations are incorrect, or, at least, not precise. Their usage implies that the integration is carried out along a closed contour which represents the path of the process. According to all that was previously explained, the work exchanged during a cycle in hydrostatic system is calculated as a simple difference between *two single integrals*, and *not as a contour integral*. The conclusion about the incorrectness of this symbol is obtained also from the geometrical meaning of the line integrals along coordinates (of the second type) [7], which essentially differs from the geometrical meaning of a simple Riemann integral (or a difference between two Riemann integrals).

Having all this in mind, it seems necessary (or, at least convenient) to introduce an alternative symbol for the total balance of work during a cycle that takes place in a hydrostatic system. In spite of the notation of the form (47), for the total balance of work, the following symbols may be used:

$$\int_V PdV \qquad (45)$$

or

$$\int_\leftrightarrow PdV \qquad (46)$$

These symbols clearly indicate that the integration is performed along the V axis (the closed "contour" of integration is, in fact, a segment of the V axis).

Namely, in case of a simple, hydrostatic system, it is not necessary to appeal on the generalization of Riemann integral, which is necessary for more complicated systems.

If the process takes place in a nonhydrostatic system, for which the element of work is given by:

$$d'w = -PdV + \sum_i Y_i dX_i \qquad (47)$$

than, really, the linear differential form of the type:

$$-PdV + \sum_i Y_i dX_i \qquad (48)$$

may be integrated along a closed contour that represents the given process. In this case, the generalization of Riemann integral is inevitable. It is necessary to point out that in the last case, it is the *general form* of the line integral of the second type (along coordinates) [2].

CONCLUSIONS

According to the rigorous mathematical treatment, appealing on the exact definitions of the Riemann and line integrals, it can be concluded that in the case of a hydrostatic system, as it was pointed out, the total balance of work can not be represented by a line integral. Therefore, notations of the type:

$$\oint PdV$$

are incorrect, or, at least, not precise. Having in mind that thermodynamic treatment of such systems requires a rigorous mathematical apparatus and approach, such imprecise formulations (notations) of general principles

should be replaced by (for instance) notations of the following (as suggested) types:

$$\int\limits_{\overset{\leftrightarrow}{V}} P dV \;,\; \int\limits_{\leftrightarrow} P dV$$

or similar.

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Р е з и м е

ЗА ЗНАЧЕЊЕТО НА ИЗРАЗИТЕ ОД ОБЛИК $\oint dF = 0$ И ФУНКЦИИТЕ НА СОСТОЈБАТА И ПАТОТ ВО ХЕМИСКАТА ТЕРМОДИНАМИКА

I. Математичкиот формализам и вистинското значење на линиските интеграли во хемиската термодинамика – внатрешна енергија и работа

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Клучни зборови: линиски интеграли; линеарни диференцијални форми; функции на состојбата; функции на патот; термодинамички системи; кружни процеси; внатрешна енергија; работа

Дискутирани се математичките аспекти на концептите за функции на состојбата и функции на патот на процесите. Укажано е на неправилноста на ползување нотации од обликот $\int d'_M$ во случај на хидростатички системи и предложена е алтернативна ознака за севкупниот биланс на работата (физичка величина која не е функција на состојбата на системите) во ваков случај. Применета е Green-овата формула на типичен термодинамички случај како доказ за независноста на вредноста на криволинискиот интеграл од втор вид (по координати) од линеарен диференцијален израз од патот на интеграцијата во случај кога линеарниот диференцијален израз е тотален диференцијал на некоја функција на состојбата.