Section A. Nomenclature Topics

Part III. Fist Law of Thermodynamics

Chapter 9. Calculus Methods

LECTURE 10. FUNCTIONS BY PFAFF

§ 1.11. Application of calculus to thermodynamics

From the equations of

$$dq = du + dl\,. \tag{2.17}$$

$$dl = pdv\,. \tag{2.18}$$

[113, pp. 29-32]

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We get the first law of thermodynamics given in the view of

[113, p. 29, (2.25)]

$$dq = du + pdv\,. \tag{2.25}$$

From

$$dq = di - pdv - vdp + pdv = di - vdp\,, \tag{2.22}$$

[113, p. 29, (2.26)]

$$dq = di - vdp\,. \tag{2.26}$$

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In mathematics they are **functions by Pfaff of two variable values**. The general view of these functions is [113, p. 29, (2.27)]

$$d\Phi = M(x,\ y)dx + N(x,\ y)dy\,. \tag{2.27}$$

for two and

$$d\Phi = X_1 dx_1 + X_2 dx_2 + X_3 dx_3 + \ldots + X_n dx_n\,.$$

for n – independent variables. Here $x_1,\ x_2,\ x_3,\ \ldots,\ x_n$ – independent variables, and $M(x,\ y),\ N(x,\ y),\ X_1,\ X_2,\ X_3,\ \ldots,\ X_n$ – functions of these variables.

For instance, pressure p and specific volume v are the independent variables, and then enthalpy i is a function of p and v

$$i = f_{pv}(p,\ v).$$

That means that at some point with the parameters of p and v we will have a certain value of the function i. At the same time, for instance, work is not a function of the same independent variables, i.e. (that is) for some certain values of p and v one cannot tell what the work would be equaled to.

In mathematics there distinguished two kinds (types, sorts) of the functions by **Pfaff**. The **first kind –** $d\Phi$ **is the complete differential of some certain function of** $d\Phi(x,\ y)$. In this case **the equality (condition by Euler) is realized** (implemented, fulfilled, carried into effect, accomplished, met) [113, p. 30, (2.28)]

$$\frac{\partial M(x,\ y)}{dy} = \frac{\partial N(x,\ y)}{dx}\,. \tag{2.28}$$

Such functions in mathematics are called **functions of point**, and in thermodynamics – **functions of state**.

For example, temperature is a function of a state of such independent parameters as pressure and specific volume. That means that in any state, which is characterized with the parameters of p and v, the temperature has quite a certain value, i.e. a function of $T = f_T(p,\ v)$ exists.

The **second kind of the Pfaff functions –** $d\Phi$ **is not the complete differential of the function of** $d\Phi(x,\ y)$. In this case **the equality (condition by Euler (2.28)) is not realized** (implemented, fulfilled, carried into effect, accomplished, met) [113, p. 30, (2.29)]

$$\frac{\partial M(x,\ y)}{dy} \neq \frac{\partial N(x,\ y)}{dx}. \qquad (2.29)$$

The functions by Pfaff of the second kind are called functions of line in mathematics, and in thermodynamics – **functions of process**.

The complete differential of the function of Φ is notated (written, put) down in the view of [113, p. 30, (2.30)]

$$d\Phi = \frac{\partial \Phi}{\partial x} dx + \frac{\partial \Phi}{\partial y} dy. \qquad (2.30)$$

Let us show that if (2.30) is the complete differential, then the equation of (2.28) realizes.

Comparing (2.30) and (2.27), we find [113, p. 30, (2.31)]

$$M(x,\ y) = \frac{\partial \Phi}{\partial x}, \qquad N(x,\ y) = \frac{\partial \Phi}{\partial y}. \qquad (2.31)$$

After differentiating the first expression form (2.31) with respect to y, and the second with respect to x, we will get [113, p. 30, (2.32)]

$$\frac{\partial M(x,\ y)}{\partial y} = \frac{\partial^2 \Phi}{\partial x \partial y}, \quad \text{and} \quad \frac{\partial N(x,\ y)}{\partial x} = \frac{\partial^2 \Phi}{\partial y \partial x}. \qquad (2.32)$$

From (2.32) we get (2.28). From here we can come to conclusion, that the condition of (2.28) is necessary for the existence of the complete differential of the function of $\Phi(x,\ y)$.

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In case if $d\Phi$ is the complete differential of some function of $F(x,\ y)$, then the value of the integral does not depend upon the way of integration

$$\int_1^2 d\Phi = \int_1^2 dF(x,\ y).$$

Integrating, we will get

$$\Phi_2 - \Phi_1 = F(x_2,\ y_2) - F(x_1,\ y_1).$$

$$\oint d\Phi = 0.$$

Functions by **Pfaff** of the second kind can be integrated only if one of the independent variables becomes a function of the other, i.e. if, for instance,

$$y = f_y(x).$$

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The relation of (2.27) then can be deduced to the view of

$$d\Phi = F(x)dx.$$

The result will be

$$\Phi = \int_1^2 F(x)dx \text{ for a process and}$$

$$\Phi = \oint F(x)dx \neq 0 \text{ for a cycle.}$$

The work of a process of l, available work of l_0, and heat of the process of q are the functions of the process. These values in pv $(l$ and $l_0)$ and Ts (q) coordinates are determined by the area under the curve of the process and depend upon the way of the process. Differentials of these values are not the complete differentials. There should be used the sign of δ.

In the equation (2.25) there is q

For some independent parameters of x and y [113, p. 31, (2.33), (2.34)]

$$du = \frac{\partial u}{\partial x} dx + \frac{\partial u}{\partial y} dy, \tag{2.33}$$

$$dv = \frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial y} dy. \tag{2.34}$$

Substituting (2.33) and (2.34) into (2.25), we will get

$$dq = \frac{\partial u}{\partial x} dx + \frac{\partial u}{\partial y} dy + p\left(\frac{\partial v}{\partial x} dx + \frac{\partial v}{\partial y} dy\right)$$

or

$$dq = M(x,\ y)dx + N(x,\ y)dy,$$

where [113, p. 32, (2.35), (2.36)]

$$M(x,\ y) = \frac{\partial u}{\partial x} + p\frac{\partial v}{\partial x}, \tag{2.35}$$

$$N(x,\ y) = \frac{\partial u}{\partial y} + p\frac{\partial v}{\partial y}. \tag{2.36}$$

Differentiating (2.35) and (2.36) with respect to y and x correspondingly

$$\frac{\partial M(x,\ y)}{\partial y} = \frac{\partial^2 u}{\partial x \partial y} + \frac{\partial p}{\partial y}\frac{\partial v}{\partial x} + p\frac{\partial^2 v}{\partial x \partial y}, \tag{2.35a}$$

$$\frac{N(x,\ y)}{\partial x} = \frac{\partial^2 u}{\partial y \partial x} + \frac{\partial p}{\partial x}\frac{\partial v}{\partial y} + p\frac{\partial^2 v}{\partial y \partial x}. \tag{2.36a}$$

Making transformations

$$\frac{\partial M(x,\ y)}{\partial y} - \frac{N(x,\ y)}{\partial x} = \frac{\partial^2 u}{\partial x \partial y} + \frac{\partial p}{\partial y}\frac{\partial v}{\partial x} + p\frac{\partial^2 v}{\partial x \partial y} - \left(\frac{\partial^2 u}{\partial y \partial x} + \frac{\partial p}{\partial x}\frac{\partial v}{\partial y} + p\frac{\partial^2 v}{\partial y \partial x}\right).$$

After rearranging

$$\frac{\partial M(x,\ y)}{\partial y} - \frac{N(x,\ y)}{\partial x} = \frac{\partial p}{\partial y}\frac{\partial v}{\partial x} - \frac{\partial p}{\partial x}\frac{\partial v}{\partial y} = D.$$

This is the **determinant by Jacoby (Jacobean)**

$$D = \begin{vmatrix} \frac{\partial v}{\partial x} & \frac{\partial p}{\partial x} \\ \frac{\partial v}{\partial y} & \frac{\partial p}{\partial y} \end{vmatrix}.$$

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[113, p. 29-32]