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Mathematical Approach to Thermodynamical System

Seminar Paper*

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Abstract: The present paper reports the new energy equation (TdS equation) for thermodynamic system using mathematical formulation. New TdS formula contains C_p (specific heat at constant pressure) and C_v (specific heat at constant volume). We have also discussed about the change in internal energy with respect to pressure and it will be treated for ideal gas as well as real gases. The internal energy of a system can be understood by examining the simplest possible system: an ideal gas. Because the particles in an ideal gas do not interact, this system has no potential energy. The internal energy of an ideal gas is therefore the sum of the kinetic energies of the particles in the gas. The internal energy of systems that is more complex than an ideal gas can't be measured directly. In the present work we have observed that the internal energy of the system depend upon pressure developed in. We can therefore monitor changes in the internal energy of a system by watching what happens to the pressure of the system. We can conclude that the change in the internal energy of a system with respect to pressure at constant is inversely proportional to volume elastic constant (E).

Keywords: TdS equation, C_p, C_v, Internal energy, Volume elastic constant.

1. Introduction

A thermodynamic potential is a scalar quantity used to represent the thermodynamic state of a system. It is very basic needs of thermodynamic and is useful to thermal energy. The concept of thermodynamic potentials was introduced by Pierre Duhem in 1886. Josiah Willard Gibbs in his papers used the term fundamental functions. One main thermodynamic potential that has a physical interpretation is the internal energy U. It is the energy of configuration of a given system of conservative forces and only has meaning with respect to a defined set of parameter. One of the thermodynamic properties of a system is its internal energy (E) which is the sum of the kinetic and potential energies of the particles that form the system. Internal energy of the system changes with pressure in constant temperature. The internal energy of systems that is more complex than an ideal gas can't be measured directly. But the internal energy of the system is still proportional to its temperature. We can therefore monitor changes in the internal energy of a system by watching what happens to the temperature of the system. Whenever the temperature of the system increases we can conclude that the internal energy of the system has also increased.

1.1. Mathematical Formulation

Entropy is the fundamental property of the thermodynamically system.Here we take the entropy of the thermodynamically system is the function of volume and pressure. In this mathematical formulation we have to find out the energy equation

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(TdS) in the form of specific heats (C_P, C_V) at constant pressure and temperature respectively. It is clear the energy of the thermodynamically system is changes with respect to the specific heats.

Section First TdS Equation : Let us consider entropy is the function of volume and temperature $S = S(V, P)$. Taking derivative of above function we get

$$dS = \left(\frac{\partial S}{\partial V}\right)_P dV + \left(\frac{\partial S}{\partial P}\right)_V dP$$
$$TdS = T\left(\frac{\partial S}{\partial V}\right)_P dV + T\left(\frac{\partial S}{\partial P}\right)_V dP$$
$$TdS = T\left(\frac{\partial S}{\partial T}\frac{\partial T}{\partial V}\right)_P dV + T\left(\frac{\partial S}{\partial T}\frac{\partial T}{\partial P}\right)_V dP$$
$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P\left(\frac{\partial T}{\partial V}\right)_P dV + T\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial T}{\partial P}\right)_V dP$$

We know

$$T\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P \text{ and } T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V$$
$$TdS = \left(\frac{\partial Q}{\partial T}\right)_P\left(\frac{\partial T}{\partial V}\right)_P dV + \left(\frac{\partial Q}{\partial T}\right)_V\left(\frac{\partial T}{\partial P}\right)_V dP$$
$$\left(\frac{\partial Q}{\partial T}\right)_P = C_P \text{ specific heat at constant pressure}$$
$$\left(\frac{\partial Q}{\partial T}\right)_V = C_V \text{ specific heat at constant pressure}$$
$$TdS = C_P\left(\frac{\partial T}{\partial V}\right)_P dV + C_V\left(\frac{\partial T}{\partial P}\right)_V dP$$
$$TdS = C_P\left(\frac{\partial T}{\partial V}\right)_P dV + C_V\left(\frac{\partial T}{\partial P}\right)_V dP$$
$$TdS = C_P\left(\frac{\partial T}{\partial V}\right)_P dV + C_V\left(\frac{\partial T}{\partial P}\right)_V dP$$
$$TdS = \frac{C_P}{\left(\frac{\partial V}{\partial T}\right)_P} dV + \frac{C_V}{\left(\frac{\partial P}{\partial T}\right)_P} dP \tag{1}$$

Using Maxwell Fourth Equation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$ we have

$$TdS = \frac{C_P}{-\left(\frac{\partial S}{\partial P}\right)_T} dV + \frac{C_V}{\left(\frac{\partial S}{\partial V}\right)_T} dP$$
$$TdS = -C_P\left(\frac{\partial P}{\partial S}\right)_T dV + C_V\left(\frac{\partial V}{\partial S}\right)_T dP \tag{2}$$

2. Change of Internal Energy of the Thermodynamically System with Respect to the Pressure in Constant Temperature

Using the thermodynamics first and second law equation $dQ = dU + PdV$, $dQ = TdS$, $TdS = dU + PdV dS = (dU + PdV)/T$ using Maxwell Fourth Equation

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$
$$\frac{1}{T}\left(\frac{\partial U + P\partial V}{\partial P}\right) = -\left(\frac{\partial V}{\partial T}\right)_P$$
$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)P - \left(\frac{\partial V}{\partial P}\right)T \tag{3}$$

Using above equation For Ideal gas $PV = RT$, $V = \frac{RT}{P}$, $\frac{\partial V}{\partial T} = \frac{R}{P}$, $\frac{\partial V}{\partial P} = -\frac{RT}{P^2}$, Equation (3) becomes

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{R}{P}\right) - P\left(-\frac{RT}{P^2}\right)$$
$$\left(\frac{\partial U}{\partial P}\right)_T = -\frac{RT}{P} + \frac{RT}{P}$$
$$\left(\frac{\partial U}{\partial P}\right)_T = 0 \tag{4}$$

Using equation (3) For Real Gas

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$
$$\frac{\partial V}{\partial T}\left(P + \frac{a}{V^2}\right) + (V - b)\left(0 - \frac{2a}{V^3}\frac{\partial V}{\partial T}\right) = R$$
$$\frac{\partial V}{\partial T}\left[\left(P + \frac{a}{V^2}\right) - (V - b)\left(\frac{2a}{V^3}\right)\right] = R$$
$$\frac{\partial V}{\partial T}\left[\left(P - \frac{a}{V^2}\right) + \left(\frac{2ab}{V^3}\right)\right] = R$$
$$\left(\frac{\partial V}{\partial T}\right) = \frac{R}{\left(P - \frac{a}{V^2}\right) + \left(\frac{2ab}{V^3}\right)}$$
$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$
$$\frac{\partial V}{\partial P}\left(P + \frac{a}{V^2}\right) + (V - b)\left(0 - \frac{2a}{V^3}\frac{\partial V}{\partial P}\right) = 0$$
$$\frac{\partial V}{\partial P}\left[\left(P + \frac{a}{V^2}\right) - (V - b)\left(\frac{2a}{V^3}\right)\right] = 0$$
$$\frac{\partial V}{\partial P}\left[\left(P - \frac{a}{V^2}\right) + \left(\frac{2ab}{V^3}\right)\right] = 0$$
$$\frac{\partial V}{\partial P} = 0$$

Equation (3) becomes

$$\left(\frac{\partial U}{\partial P}\right)_T = -\frac{R}{\left(P - \frac{a}{V^2}\right) + T\left(\frac{2ab}{V^3}\right)} \tag{5}$$

$\left(\frac{2ab}{V^3}\right)$ is the small quantity so it can be drop from equation 5 and than write

$$\left(\frac{\partial U}{\partial P}\right)_T = -\frac{R}{\left(P - \frac{a}{V^2}\right)} \tag{6}$$

If increase the pressure of the system their internal energy will be decrease that is the basic mechanism which we have describe in the boyle law, So this result shows that internal energy of the system will be positive with increase in volume and decrease in pressure. Let us consider following function $V = V(P, T)$. Here we take volume as a function of pressure and temperature. Taking derivative of above function we get

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$$

at constant volume $dV = 0$ so $0 = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP$

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right) \tag{7}$$

using Equation (3)

$$\begin{aligned}
\left(\frac{\partial U}{\partial P}\right)_T &= -T\left(\frac{\partial V}{\partial T}\right)P - \left(\frac{\partial V}{\partial P}\right)T \\
\left(\frac{\partial U}{\partial P}\right)_T &= -T\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right) - \left(\frac{\partial V}{\partial P}\right)_T \\
\left(\frac{\partial U}{\partial P}\right)_T &= \left(\frac{\partial V}{\partial P}\right)_T\left[T\left(\frac{\partial P}{\partial T}\right) - P\right] \\
\left(\frac{\partial U}{\partial P}\right)_T &= \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] \\
\left(\frac{\partial U}{\partial P}\right)_T &= \frac{V}{V\left(\frac{\partial V}{\partial P}\right)_T}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] \qquad (8)
\end{aligned}$$

E is the volume elastic constant which is in form of $E = -V\left(\frac{\partial V}{\partial P}\right)_T$ so equation (8) is

$$\left(\frac{\partial U}{\partial P}\right)_T = \frac{V}{E}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] \qquad (9)$$

Using Maxwell equation

$$\begin{aligned}
\left(\frac{\partial P}{\partial T}\right)_V &= \left(\frac{\partial S}{\partial V}\right)_T \\
\left(\frac{\partial U}{\partial P}\right)_T &= \frac{1}{\left(\frac{\partial V}{\partial P}\right)_T}\left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right] \\
\left(\frac{\partial U}{\partial P}\right)_T &= \frac{V}{V\left(\frac{\partial V}{\partial P}\right)_T}\left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right] \\
\left(\frac{\partial U}{\partial P}\right)_T &= \frac{V}{E}\left[T\left(\frac{\partial S}{\partial V}\right)_T - P\right] \qquad (10)
\end{aligned}$$

For ideal gas $PV = RT$, $P = \frac{RT}{V}$, $\frac{\partial P}{\partial T} = \frac{R}{V}$. Than equation $\left(\frac{\partial U}{\partial P}\right)_T = \frac{1}{E}[-T\left(\frac{\partial P}{\partial T}\right)_V + P]$ reduced to $\left(\frac{\partial U}{\partial P}\right)_T = \frac{V}{E}[-\frac{RT}{V} + P]$; $\left(\frac{\partial U}{\partial P}\right)_T = 0$. Let us again consider

$$\begin{aligned}
V &= V(P,T) \\
dV &= \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP
\end{aligned}$$

at constant volume $dV = 0$ so

$$\begin{aligned}
0 &= \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \\
\left(\frac{\partial V}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right) \qquad (11)
\end{aligned}$$

using Equation (3)

$$\begin{aligned}
\left(\frac{\partial U}{\partial P}\right)_T &= -T\left(\frac{\partial V}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial P}\right)_T \\
\left(\frac{\partial U}{\partial P}\right)_T &= -T\left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right) \\
\left(\frac{\partial U}{\partial P}\right)_T &= -\left(\frac{\partial V}{\partial T}\right)_P\left[T - P\left(\frac{\partial T}{\partial P}\right)\right] \\
\left(\frac{\partial U}{\partial P}\right)_T &= -\frac{1}{\left(\frac{\partial V}{\partial T}\right)_P}\left[T - P\left(\frac{\partial T}{\partial P}\right)_V\right] \\
\left(\frac{\partial U}{\partial P}\right)_T &= -\frac{V}{V\left(\frac{\partial V}{\partial P}\right)_T}\left[T - P\left(\frac{\partial T}{\partial P}\right)_V\right] \qquad (12)
\end{aligned}$$

E is the volume elastic constant which is in form of $E = -V\left(\frac{\partial V}{\partial P}\right)_T$ so equation (8) is

$$\left(\frac{\partial U}{\partial P}\right)_T = \frac{V}{E}\left[T - P\left(\frac{\partial T}{\partial P}\right)_V\right] \tag{13}$$

For ideal gas $PV = RT$, $T = \frac{PV}{R}$, $\frac{\partial T}{\partial P} = \frac{V}{R}$ Than equation

$$\left(\frac{\partial U}{\partial P}\right)_T = \frac{V}{E}\left[T - \frac{PV}{R}\right]$$
$$\left(\frac{\partial U}{\partial P}\right)_T = \frac{V}{E}\left[T - \frac{RT}{R}\right]$$
$$\left(\frac{\partial U}{\partial P}\right)_T = \frac{V}{E}[T - T]$$
$$\left(\frac{\partial U}{\partial P}\right)_T = 0$$

3. Conclusion

In the present work we have to calculate new kind of TdS equation for themodyanamically system. In the above mathematical formulation TdS function is directly proportional to C_p (specific heat at constant pressure) and C_v (specific heat at constant volume). We have also discussed about the change in internal energy with pressure in constant temperature and obtain the new $\left(\frac{\partial U}{\partial P}\right)_T$ equation. For the ideal gas both the term $\left(\frac{\partial U}{\partial P}\right)_T$ tend to zero. The ideal gas retains its property that means there is no change observed whichever thermodynamically variable change be. In the real gas system the $\left(\frac{\partial U}{\partial P}\right)_T$ function is inversely proportional to pressure and elastic constant.

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