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Derivation of the Third TdS Equation in Thermodynamics

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Abstract

P&V Independent involves the application of T&V independent together with the Application of second law of thermodynamics. The third TdS equation together with the first and second TdS equations has been known to many as the “tedious equations” due to a lot of derivations with resemblances involved. The TdS equations enables us to calculate the change of entropy during various reversible processes in terms of either dV and dT, or dP and dT, or dV and dP, and even in terms of directly measurable quantities such as the coefficient of expansion and the bulk modulus. This Manuscript involves another way of deriving the Thirds TdS equation applying the second law of thermodynamics together with equations already derived and introduced from the derivations of T&V which is also an application of the second law of thermodynamics.

Keywords

Putting, Substituting, Eqn, Constant

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1. Introduction

Thermodynamics is a branch of physics concerned with heat and temperature and their relation to energy and work. It defines macroscopic variables, such as internal energy, entropy, and pressure that partly describe a body of matter or radiation. [24] The basic idea is that objects are made up of atoms and molecules, which are in ceaseless motion. The faster the motion the hotter the object. However, thermodynamics deals only with the largescale response of a system, i.e. response that can be observed and measured, to heat flow.

Thermodynamics is a collection of useful mathematical relations between quantities, every one of which is independently measurable. Although thermodynamics tells us nothing whatsoever of the microscopic explanation of macroscopic changes, it is useful because it can be used to quantify many unknowns. Thermodynamics is useful precisely because some quantities are easier to measure than others. The laws of thermodynamics provide an elegant mathematical expression of some empirically-discovered facts of nature. The principle of energy conservation allows the energy requirements for processes to be calculated. The principle of increasing entropy (and the resulting free-energy minimization) allows predictions to be made of the extent to which those processes may proceed. Thermodynamics deals with some very abstract quantities, and makes deductions using mathematical relations. In this, it is a little like mathematics itself, which, according to Bertrand Russell, is a domain where you never know a) what you’re talking about, nor b) whether what you’re saying is true. However, thermodynamics is trusted as a reliable source of information about the real world, precisely because it has delivered the goods in the past. Its ultimate justification is that it works. Confusion in thermodynamics can easily result if terms are not properly defined. There is no room for the loose use of words in this subject.

The second law of thermodynamics is arguably the most

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enigmatic and provocative fundamental statement of relevance to engineering, physics, chemistry and biology. It is instructive to recall that the discovery of this profound principle of nature originally emerged from the practical concerns of nineteenth century industrialists who desired to increase the efficiency of steam engines. Although the second law of thermodynamics may be stated in a myriad of ways. The energy of the universe is constant. The entropy of the universe seeks a maximum. Thus, the second law may be summarized by the deceptively simple inequality, $\Delta \geq 0$ *S Univ,* pertaining to the increase in the entropy of the universe (or of any isolated entity) produced as a result of spontaneous (irreversible) processes. Although there is no question regarding the wide ranging implications of this and other statements of the second law, it is important to note that none of these statements can in themselves be used to quantify the excess entropy produced as the result of a given irreversible process.

*(*www.yourdictionary.com/thermodynamic*).* The three TdS equations have been known to generations of students as the "tedious equations" − though they are not at all tedious to a true lover of thermodynamics, because, among other things, they enable us to calculate the change of entropy during various reversible processes in terms of either dV and dT, or dP and dT, or dV and dP, and even in terms of directly measurable quantities such as the coefficient of expansion and the bulk modulus. We can express entropy in terms of any two of PVT. [1] This Manuscript involves another method or way of deriving the Thirds TdS equation applying the second law of thermodynamics together with equations already derived and introduced from the derivations of T&V which is also an application of the second law of thermodynamics.

2. Methodology

This section involves derivation of p and V independent which is an application of the second law of thermodynamics.

The P & V Independent show that

$$Tds = C_{p}\left(\frac{\partial T}{\partial V}\right)_{p} dv + C_{v}\left(\frac{\partial T}{\partial P}\right)_{v} dp$$

Solution

The energy difference between two neighboring equilibrium states in which the pressure and volume differs by dp and dv is given as

$$du = \left(\frac{\partial u}{\partial p}\right)_{v} dp + \left(\frac{\partial u}{\partial v}\right)_{p} dv \tag{1}$$

In equation (1) the partial derivatives do not involve any properties other than those introduced in $T \,\&\, V$ independent i.e.

$$du = \left(\frac{\partial u}{\partial T}\right)_{v} dT + \left(\frac{\partial u}{\partial v}\right)_{T} dv \tag{2}$$

Then since

$$dT = \left(\frac{\partial T}{\partial p}\right)_{v} dp + \left(\frac{\partial T}{\partial v}\right)_{p} dv \tag{3}$$

Putting eqn. (3) into eqn. (2) we've

$$du = \left(\frac{\partial u}{\partial T}\right)_{v}\left[\left(\frac{\partial T}{\partial p}\right)_{v} dp + \left(\frac{\partial T}{\partial v}\right)_{p} dv\right] + \left(\frac{\partial u}{\partial v}\right)_{T} dv \tag{4}$$

$$du = \left(\frac{\partial u}{\partial T}\right)_{v}\left(\frac{\partial T}{\partial p}\right)_{v} dp + \left(\frac{\partial u}{\partial T}\right)_{v}\left(\frac{\partial T}{\partial v}\right)_{p} dv + \left(\frac{\partial u}{\partial v}\right)_{T} dv \tag{5}$$

$$du = \left(\frac{\partial u}{\partial T}\right)_{v}\left(\frac{\partial T}{\partial p}\right)_{v} dp + \left[\left(\frac{\partial u}{\partial T}\right)_{v}\left(\frac{\partial T}{\partial v}\right)_{p} + \left(\frac{\partial u}{\partial v}\right)_{T}\right] dv \tag{6}$$

comparing eqn (1) with eqn (6) we've

$$\left(\frac{\partial u}{\partial p}\right)_{v} dp = \left(\frac{\partial u}{\partial T}\right)_{v}\left(\frac{\partial T}{\partial p}\right)_{v} dp \Rightarrow \left(\frac{\partial u}{\partial p}\right)_{v} = \left(\frac{\partial u}{\partial T}\right)_{v}\left(\frac{\partial T}{\partial p}\right)_{v} \tag{7}$$

also

$$\left(\frac{\partial u}{\partial v}\right)_{p} = \left(\frac{\partial u}{\partial T}\right)_{v}\left(\frac{\partial T}{\partial v}\right)_{p} + \left(\frac{\partial u}{\partial v}\right)_{T} \tag{8}$$

Recall that

$$C_{v} = \left(\frac{\partial u}{\partial T}\right) \tag{9}$$

putting eqn (9) into eqn (7) we've

$$\left(\frac{\partial u}{\partial p}\right)_{v} = C_{v}\left(\frac{\partial T}{\partial p}\right)_{v} \tag{10}$$

recall that

$$h = u + pv \tag{11}$$

$$dh = du + pdv + vdp \tag{12}$$

at constant volume and constant pressure

$dv = 0 \,\&\, dp = 0 \;\; \therefore eqn(12)$ *becomes*

$$dh = du \tag{13}$$

putting eqn(13) into eqn (8) we've

$$\left(\frac{\partial h}{\partial v}\right)_p=\left(\frac{\partial h}{\partial T}\right)_v\left(\frac{\partial T}{\partial v}\right)_p+\left(\frac{\partial h}{\partial v}\right)_T \tag{14}$$

at constant temperature $\left(\frac{\partial h}{\partial v}\right)_T=0$

$\therefore$ *eqn*(14) *becomes*

$$\left(\frac{\partial h}{\partial v}\right)_p=\left(\frac{\partial h}{\partial T}\right)_v\left(\frac{\partial T}{\partial v}\right)_p \tag{15}$$

recall that

$$C_p=\left(\frac{\partial h}{\partial T}\right)_v \tag{16}$$

Putting eqn (16) into eqn (15) we've

$$\left(\frac{\partial h}{\partial v}\right)_p=C_p\left(\frac{\partial T}{\partial v}\right)_p \tag{17}$$

From eqn (13) substituting *dh* for *du* ineqn (17) we've

$$\left(\frac{\partial u}{\partial v}\right)_p=C_p\left(\frac{\partial T}{\partial v}\right)_p \tag{18}$$

Hence putting eqn (10) & (18) into eqn (1) we've

$$du=C_v\left(\frac{\partial T}{\partial p}\right)_v dp+C_p\left(\frac{\partial T}{\partial v}\right)_p dv \tag{19}$$

From the combined first and second law of thermodynamics we've

$$ds=\frac{1}{T}\left(du+pdv\right) \tag{20}$$

At constant volume process $dv=0$ hence eqn (20) becomes

$$ds=\frac{1}{T}du \tag{21}$$

Putting eqn (19) into eqn (21) we've

$$ds=\frac{1}{T}\left[C_v\left(\frac{\partial T}{\partial p}\right)_v dp+C_p\left(\frac{\partial T}{\partial v}\right)_p dv\right] \tag{22}$$

$$ds=\frac{C_v}{T}\left(\frac{\partial T}{\partial p}\right)_v dp+\frac{C_p}{T}\left(\frac{\partial T}{\partial v}\right)_p dv \tag{23}$$

But we can also write

$$ds=\left(\frac{\partial s}{\partial p}\right)_v dp+\left(\frac{\partial s}{\partial v}\right)_p dv \tag{24}$$

Comparing eqn (23) with eqn (24) we've

$$\left(\frac{\partial s}{\partial p}\right)_v=\frac{C_v}{T}\left(\frac{\partial T}{\partial p}\right)_v \tag{25}$$

$$\left(\frac{\partial s}{\partial v}\right)_p=\frac{C_p}{T}\left(\frac{\partial T}{\partial v}\right)_p \tag{26}$$

differentiating eqn (25) partially w.r.t v we've

$$\frac{\partial^2 s}{\partial v\partial p}=\frac{C_v}{T}\frac{\partial}{\partial v}\left(\frac{\partial T}{\partial p}\right)_v=\frac{C_v}{T}\frac{\partial^2 T}{\partial v\partial p} \tag{27}$$

differentiating eqn (26) partially w.r.t p we've

$$\frac{\partial}{\partial p}\left(\frac{\partial s}{\partial v}\right)_p=\frac{\partial^2 s}{\partial p\partial v}=\frac{\partial}{\partial p}\left(\frac{C_p}{T}\left(\frac{\partial T}{\partial v}\right)_p\right)=\frac{C_p}{T}\frac{\partial^2 T}{\partial p\partial v} \tag{28}$$

equating the R.H.S of eqn (27) &(28) we've

$$\frac{C_v}{T}\frac{\partial^2 T}{\partial v\partial p}=\frac{C_p}{T}\frac{\partial^2 T}{\partial p\partial v} \tag{29}$$

From eqn (29)

$$\Rightarrow\frac{C_v}{T}=\frac{C_p}{T}$$

$$\therefore C_v=C_p \tag{30}$$

From eqn (23) we've

$$ds=\frac{C_v}{T}\left(\frac{\partial T}{\partial p}\right)_v dp+\frac{C_p}{T}\left(\frac{\partial T}{\partial v}\right)_p dv \tag{31}$$

Multiplying through eqn (31) by T we've

$$Tds=C_v\left(\frac{\partial T}{\partial p}\right)_v dp+C_p\left(\frac{\partial T}{\partial v}\right)_p dv \tag{32}$$

$$Tds=C_p\left(\frac{\partial T}{\partial v}\right)_p dv+C_v\left(\frac{\partial T}{\partial p}\right)_v dp \tag{33}$$

Hence eqn(33) *is called the third Tds equation.*

Laws of Thermodynamics

There are four basic laws of Thermodynamics, The four laws of thermodynamics define fundamental physical quantities (temperature, energy, and entropy) that characterize thermodynamic systems at thermal equilibrium. The laws describe how these quantities behave under various circumstances, and forbid certain phenomena (such as perpetual motion). The four laws of thermodynamics are: [15-19].

a. Zeroth law of thermodynamics: If two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with each other. This law helps define the concept of temperature.

b. First law of thermodynamics: When energy passes, as work, as heat, or with matter, into or out from a system, the system's internal energy changes in accord with the law of conservation of energy. Equivalently, perpetual motion machines of the first kind (machines that produce work with no energy input) are impossible.

c. Second law of thermodynamics: In a natural thermodynamic process, the sum of the entropies of the interacting thermodynamic systems increases. Equivalently, perpetual motion machines of the second kind (machines that spontaneously convert thermal energy into mechanical work) are impossible.

d. Third law of thermodynamics: The entropy of a system approaches a constant value as the temperature approaches absolute zero. [16] With the exception of non-crystalline solids (glasses) the entropy of a system at absolute zero is typically close to zero, and is equal to the natural logarithm of the product of the quantum ground states.

Applied Fields of Thermodynamics

Thermodynamics has several Application is different fields, amongst which we've

a. Atmospheric thermodynamics
b. Biological thermodynamics
c. Black hole thermodynamics
d. Chemical thermodynamics
e. Classical thermodynamics
f. Equilibrium thermodynamics
g. Industrial ecology
h. Maximum entropy thermodynamics
i. Non-equilibrium thermodynamics
j. Philosophy of thermal and statistical physics
k. Psychrometrics
l. Quantum thermodynamics
m. Statistical thermodynamics
n. Thermoeconomics

Atmospheric thermodynamics is the study of heat -to-work transformations (and their reverse) that take place in the earth's atmosphere and manifest as weather or climate.

Atmospheric thermodynamics use the laws of classical thermodynamics, to describe and explain such phenomena as the properties of moist air, the formation of clouds, atmospheric convection, boundary layer meteorology, and vertical instabilities in the atmosphere.

Atmospheric thermodynamic diagrams are used as tools in the forecasting of storm development.

Atmospheric thermodynamics

forms a basis for cloud microphysics and convection parameterizations used in numerical weather models and is used in many climate considerations, including convective-equilibrium climate models.

Classical thermodynamics

Classical thermodynamics is the description of the states of thermodynamic systems at near-equilibrium, that uses macroscopic, measurable properties.

It is used to model exchanges of energy, work and heat based on the laws of thermodynamics.

The qualifier classical reflects the fact that it represents the first level of understanding of the subject as it developed in the 19th century and describes the changes of a system in terms of macroscopic empirical (large scale, and measurable) parameters.

A microscopic interpretation of these concepts was later provided by the development of statistical mechanics.

Statistical mechanics

Statistical mechanics, also called statistical thermodynamics, emerged with the development of atomic and molecular theories in the late 19th century and early 20th century, and supplemented classical thermodynamics with an interpretation of the microscopic interactions between individual particles or quantum-mechanical states.

This field relates the microscopic properties of individual atoms and molecules to the macroscopic, bulk properties of materials that can be observed on the human scale, thereby explaining classical thermodynamics as a natural result of statistics, classical mechanics, and quantum theory at the microscopic level.

Chemical thermodynamics

Chemical thermodynamics is the study of the interrelation of energy with chemical reactions or with a physical change of state within the confines of the laws of thermodynamics.

Equilibrium thermodynamics

Equilibrium thermodynamics is the systematic study of transformations of matter and energy in systems as they approach equilibrium. The word equilibrium implies a state of balance. In an equilibrium state there are no unbalanced potentials, or driving forces, within the system.

A central aim in equilibrium thermodynamics is given a system in a well-defined initial state, subject to accurately specified constraints, to calculate what the state of the system will be once it has reached equilibrium.

Non-equilibrium thermodynamics is a branch of thermodynamics that deals with systems that are not in thermodynamic equilibrium.

Most systems found in nature are not in thermodynamic equilibrium because they are not in stationary states, and are continuously and discontinuously subject to flux of matter and energy to and from other systems.

The thermodynamic study of non-equilibrium systems requires more general concepts than are dealt with by equilibrium thermodynamics.

Many natural systems still today remain beyond the scope of currently known macroscopic thermodynamic methods.

3. Conclusion

Equation (33) show the Third TdS equation derived in another way, the first, second and thirds TdS equations which are applications of the second law of thermodynamics can be used to calculate using method of integration, the change of entropy between one state and another, provided that the equation of state is known in order that we can evaluate the partial derivatives.

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