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CHAPTER 3: THERMO

Version: 0.3.1.1 December 21, 2011

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“Basics of Fluid Mechanics”

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DECEMBER 21, 2011

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NSY = Not Started Yet

CHAPTER 2

Review of Thermodynamics

In this chapter, a review of several definitions of common thermodynamics terms is presented. This introduction is provided to bring the student back to current place with the material.

2.1 *Basic Definitions*

The following basic definitions are common to thermodynamics and will be used in this book.

Work

In mechanics, the work was defined as

$$\text{mechanical work} = \int \mathbf{F} \cdot d\ell = \int PdV \quad (2.1)$$

This definition can be expanded to include two issues. The first issue that must be addressed, that work done on the surroundings by the system boundaries similarly is positive. Two, there is a transfer of energy so that its effect can cause work. It must be noted that electrical current is a work while heat transfer isn't.

System

This term will be used in this book and it is defined as a continuous (at least partially) fixed quantity of matter. The dimensions of this material can be changed. In this definition, it is assumed that the system speed is significantly lower than that of the speed of light. So, the mass can be assumed constant even though the true conservation law applied to the combination of mass energy (see Einstein's law). In fact for almost all engineering purpose this law is reduced to two separate laws of mass conservation and energy conservation.

Our system can receive energy, work, etc as long the mass remain constant the definition is not broken.

Thermodynamics First Law

This law refers to conservation of energy in a non accelerating system. Since all the systems can be calculated in a non accelerating systems, the conservation is applied to all systems. The statement describing the law is the following.

$$Q_{12} - W_{12} = E_2 - E_1 \quad (2.2)$$

The system energy is a state property. From the first law it directly implies that for process without heat transfer (adiabatic process) the following is true

$$W_{12} = E_1 - E_2 \quad (2.3)$$

Interesting results of equation (2.3) is that the way the work is done and/or intermediate states are irrelevant to final results. There are several definitions/separations of the kind of works and they include kinetic energy, potential energy (gravity), chemical potential, and electrical energy, etc. The internal energy is the energy that depends on the other properties of the system. For example for pure/homogeneous and simple gases it depends on two properties like temperature and pressure. The internal energy is denoted in this book as E_U and it will be treated as a state property.

The potential energy of the system is depended on the body force. A common body force is the gravity. For such body force, the potential energy is mgz where g is the gravity force (acceleration), m is the mass and the z is the vertical height from a datum. The kinetic energy is

$$K.E. = \frac{mU^2}{2} \quad (2.4)$$

Thus the energy equation can be written as

Total Energy Equation

$$\frac{mU_1^2}{2} + mgz_1 + E_{U1} + Q = \frac{mU_2^2}{2} + mgz_2 + E_{U2} + W \quad (2.5)$$

For the unit mass of the system equation (2.5) is transformed into

Specific Energy Equation

$$\frac{U_1^2}{2} + gz_1 + E_{u1} + q = \frac{U_2^2}{2} + gz_2 + E_{u2} + w \quad (2.6)$$

where q is the energy per unit mass and w is the work per unit mass. The "new" internal energy, E_u , is the internal energy per unit mass.

Since the above equations are true between arbitrary points, choosing any point in time will make it correct. Thus differentiating the energy equation with respect to time yields the rate of change energy equation. The rate of change of the energy transfer is

$$\frac{DQ}{Dt} = \dot{Q} \quad (2.7)$$

In the same manner, the work change rate transferred through the boundaries of the system is

$$\frac{DW}{Dt} = \dot{W} \quad (2.8)$$

Since the system is with a fixed mass, the rate energy equation is

$$\dot{Q} - \dot{W} = \frac{D E_U}{Dt} + mU \frac{DU}{Dt} + m \frac{D B_f z}{Dt} \quad (2.9)$$

For the case were the body force, B_f , is constant with time like in the case of gravity equation (2.9) reduced to

Time Dependent Energy Equation

$$\dot{Q} - \dot{W} = \frac{D E_U}{Dt} + mU \frac{DU}{Dt} + m g \frac{D z}{Dt} \quad (2.10)$$

The time derivative operator, D/Dt is used instead of the common notation because it referred to system property derivative.

Thermodynamics Second Law

There are several definitions of the second law. No matter which definition is used to describe the second law it will end in a mathematical form. The most common mathematical form is Clausius inequality which state that

$$\oint \frac{\delta Q}{T} \geq 0 \quad (2.11)$$

The integration symbol with the circle represent integral of cycle (therefor circle) in with system return to the same condition. If there is no lost, it is referred as a reversible process and the inequality change to equality.

$$\oint \frac{\delta Q}{T} = 0 \quad (2.12)$$

The last integral can go though several states. These states are independent of the path the system goes through. Hence, the integral is independent of the path. This observation leads to the definition of entropy and designated as S and the derivative of entropy is

$$ds \equiv \left(\frac{\delta Q}{T} \right)_{\text{rev}} \quad (2.13)$$

Performing integration between two states results in

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{\text{rev}} = \int_1^2 dS \quad (2.14)$$

One of the conclusions that can be drawn from this analysis is for reversible and adiabatic process $dS = 0$. Thus, the process in which it is reversible and adiabatic, the entropy remains constant and referred to as isentropic process. It can be noted that there is a possibility that a process can be irreversible and the right amount of heat transfer to have zero change entropy change. Thus, the reverse conclusion that zero change of entropy leads to reversible process, isn't correct.

For reversible process equation (2.12) can be written as

$$\delta Q = TdS \quad (2.15)$$

and the work that the system is doing on the surroundings is

$$\delta W = PdV \quad (2.16)$$

Substituting equations (2.15) (2.16) into (2.10) results in

$$TdS = dE_U + PdV \quad (2.17)$$

Even though the derivation of the above equations were done assuming that there is no change of kinetic or potential energy, it still remain valid for all situations. Furthermore, it can be shown that it is valid for reversible and irreversible processes.

Enthalpy

It is a common practice to define a new property, which is the combination of already defined properties, the enthalpy of the system.

$$H = E_U + PV \quad (2.18)$$

The specific enthalpy is enthalpy per unit mass and denoted as, h .

Or in a differential form as

$$dH = dE_U + dPV + P dV \quad (2.19)$$

Combining equations (2.18) the (2.17) yields

(one form of) Gibbs Equation

$$TdS = dH - VdP \quad (2.20)$$

For isentropic process, equation (2.17) is reduced to $dH = VdP$. The equation (2.17) in mass unit is

$$Tds = du + Pdv = dh - \frac{dP}{\rho} \quad (2.21)$$

when the density enters through the relationship of $\rho = 1/v$.

Specific Heats

The change of internal energy and enthalpy requires new definitions. The first change of the internal energy and it is defined as the following

Specific Volume Heat

$$C_v \equiv \left(\frac{\partial E_u}{\partial T} \right) \quad (2.22)$$

And since the change of the enthalpy involve some kind of work is defined as

Specific Pressure Heat

$$C_p \equiv \left(\frac{\partial h}{\partial T} \right) \quad (2.23)$$

The ratio between the specific pressure heat and the specific volume heat is called the ratio of the specific heat and it is denoted as, k .

Specific Heats Ratio

$$k \equiv \frac{C_p}{C_v} \quad (2.24)$$

For solid, the ratio of the specific heats is almost 1 and therefore the difference between them is almost zero. Commonly the difference for solid is ignored and both are assumed to be the same and therefore referred as C . This approximation less strong for liquid but not by that much and in most cases it applied to the calculations. The ratio the specific heat of gases is larger than one.

Equation of state

Equation of state is a relation between state variables. Normally the relationship of temperature, pressure, and specific volume define the equation of state for gases. The simplest equation of state referred to as ideal gas. and it is defined as

$$P = \rho RT \quad (2.25)$$

Application of Avogadro's law, that "all gases at the same pressures and temperatures have the same number of molecules per unit of volume," allows the calculation of a "universal gas constant." This constant to match the standard units results in

$$\bar{R} = 8.3145 \frac{kJ}{kmol K} \quad (2.26)$$

Thus, the specific gas can be calculate as

$$R = \frac{\bar{R}}{M} \quad (2.27)$$

The specific constants for select gas at 300K is provided in table 2.1.

Table -2.1. Properties of Various Ideal Gases [300K]

| Gas | Chemical Formula | Molecular Weight | $R \left[\frac{kJ}{KgK} \right]$ | $C_P \left[\frac{kJ}{KgK} \right]$ | $C_v \left[\frac{kJ}{KgK} \right]$ | k |
|-----------------|------------------|------------------|-----------------------------------|-------------------------------------|-------------------------------------|-------|
| Air | - | 28.970 | 0.28700 | 1.0035 | 0.7165 | 1.400 |
| Argon | Ar | 39.948 | 0.20813 | 0.5203 | 0.3122 | 1.667 |
| Butane | C_4H_{10} | 58.124 | 0.14304 | 1.7164 | 1.5734 | 1.091 |
| Carbon Dioxide | CO_2 | 44.01 | 0.18892 | 0.8418 | 0.6529 | 1.289 |
| Carbon Monoxide | CO | 28.01 | 0.29683 | 1.0413 | 0.7445 | 1.400 |
| Ethane | C_2H_6 | 30.07 | 0.27650 | 1.7662 | 1.4897 | 1.186 |
| Ethylene | C_2H_4 | 28.054 | 0.29637 | 1.5482 | 1.2518 | 1.237 |
| Helium | He | 4.003 | 2.07703 | 5.1926 | 3.1156 | 1.667 |
| Hydrogen | H_2 | 2.016 | 4.12418 | 14.2091 | 10.0849 | 1.409 |
| Methane | CH_4 | 16.04 | 0.51835 | 2.2537 | 1.7354 | 1.299 |
| Neon | Ne | 20.183 | 0.41195 | 1.0299 | 0.6179 | 1.667 |
| Nitrogen | N_2 | 28.013 | 0.29680 | 1.0416 | 0.7448 | 1.400 |
| Octane | C_8H_{18} | 114.230 | 0.07279 | 1.7113 | 1.6385 | 1.044 |
| Oxygen | O_2 | 31.999 | 0.25983 | 0.9216 | 0.6618 | 1.393 |
| Propane | C_3H_8 | 44.097 | 0.18855 | 1.6794 | 1.4909 | 1.126 |
| Steam | H_2O | 18.015 | 0.48152 | 1.8723 | 1.4108 | 1.327 |

From equation (2.25) of state for perfect gas it follows

$$d(Pv) = RdT \quad (2.28)$$

For perfect gas

$$dh = dE_u + d(Pv) = dE_u + d(RT) = f(T) \text{ (only)} \quad (2.29)$$

From the definition of enthalpy it follows that

$$d(Pv) = dh - dE_u \quad (2.30)$$

Utilizing equation (2.28) and substituting into equation (2.30) and dividing by dT yields

$$C_p - C_v = R \quad (2.31)$$

This relationship is valid only for ideal/perfect gases.

The ratio of the specific heats can be expressed in several forms as

C_v to Specific Heats Ratio

$$C_v = \frac{R}{k-1} \quad (2.32)$$

C_p to Specific Heats Ratio

$$C_p = \frac{kR}{k-1} \quad (2.33)$$

The specific heat ratio, k value ranges from unity to about 1.667. These values depend on the molecular degrees of freedom (more explanation can be obtained in Van Wylen "F. of Classical thermodynamics." The values of several gases can be approximated as ideal gas and are provided in Table (2.1).

The entropy for ideal gas can be simplified as the following

$$s_2 - s_1 = \int_1^2 \left(\frac{dh}{T} - \frac{dP}{\rho T} \right) \quad (2.34)$$

Using the identities developed so far one can find that

$$s_2 - s_1 = \int_1^2 C_p \frac{dT}{T} - \int_1^2 \frac{R dP}{P} = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad (2.35)$$

Or using specific heat ratio equation (2.35) transformed into

$$\frac{s_2 - s_1}{R} = \frac{k}{k-1} \ln \frac{T_2}{T_1} - \ln \frac{P_2}{P_1} \quad (2.36)$$

For isentropic process, $\Delta s = 0$, the following is obtained

$$\ln \frac{T_2}{T_1} = \ln \left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} \quad (2.37)$$

There are several famous identities that results from equation (2.37) as

Ideal Gas Isentropic Relationships

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} = \left(\frac{V_1}{V_2} \right)^{k-1} \quad (2.38)$$

The ideal gas model is a simplified version of the real behavior of real gas. The real gas has a correction factor to account for the deviations from the ideal gas model. This correction factor referred as the compressibility factor and defined as

Z deviation from the Ideal Gas Model

$$Z = \frac{PV}{RT}$$

(2.39)