

# Engineering Thermodynamics

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## §1 July 5, 2017

### §1.1 Thermodynamics

**Thermodynamics** is a branch of science which deals with equilibrium processes involving heat and work. In thermodynamics, rates are not considered. Thermodynamics constrains all processes, as it sets the limits of a system's performance.

In a closed system, we refer to the gas as a **control mass**. A force could be applied to the control mass, which is encapsulated by a **system boundary**.

Open systems on the other hand, includes pumps, turbines, compressors, refrigerators, and valves. An open system such as a water heater would have  $F_{in}$ ,  $T_{in}$ ,  $F_{out}$ , and  $T_{out}$ . Both mass and energy can cross the system boundary in an open system. The open systems we will consider will be assumed to operate in **steady-state**. That is, the accumulation term in the mass or energy balance will be zero, since it will not change with time.

Below are conversions between common temperature units:

- $T(K) = T(^{\circ}C) + 273.15$ .
- $T(R) = T(^{\circ}F) + 459.67$ .
- $T(^{\circ}F) = 1.8 \cdot T(^{\circ}C) + 32$ .
- $-273.15^{\circ}C = -459.67^{\circ}F = 0K = 0R$ .
- $\Delta T(K) = \Delta T(^{\circ}C)$ .
- $\Delta T(R) = \Delta T(^{\circ}F)$ .

## §2 July 7, 2017

### §2.1 Properties

**Properties** are independent of path. In other words, properties are independent of history. For instance, work and heat depend on how the process works. Thus, they are path dependent and are not properties. Some examples of properties include volume, temperature, pressure, mass, internal energy, enthalpy, and entropy. Properties can be further classified as intensive or extensive:

- **Intensive Properties** are independent of size. Examples include temperature and pressure. Intensive properties are usually lowercase (except temperature and pressure).
- **Extensive Properties** are dependent upon the size of the system. For example, length, mass, and volume are extensive properties. Extensive properties are usually uppercase (except mass).

To determine whether a property is intensive or extensive, we can divide the system into two equal parts with an imaginary split. Each part will have the same value of intensive properties as the original system, but only half the initial value of the extensive properties.

**Specific properties** are extensive properties divided by mass. For single phase systems, specific properties are also intensive. Examples include specific volume, specific enthalpy, specific internal energy, and specific entropy.

**Remark 2.1.** Specific gravity is the density of a substance divided by the density of water.

## §3 July 10, 2017

### §3.1 Systems

A **system** defines the volume in space in which we are applying our analysis. The boundary of the system is arbitrary. However, some choices may simplify analysis. There are three types of systems:

1. **Open Systems:** Mass and energy can cross the system boundary. Mass can flow in and out. Work is done by the surroundings on the system.
2. **Closed Systems:** Mass cannot leave the system, but energy can. Pistons and cylinders are examples of closed systems.
3. **Isolated Systems:** Neither mass nor energy can cross the system boundary.

The **state** is the value of a system's properties at any given moment. A **process** occurs when there is a change in the state. When a process starts and finishes at the same state, we have a **cycle**. There are different types of processes:

- **Isothermal:** The process occurs at a constant temperature. This usually requires adding or removing heat.
- **Isobaric:** The process occurs at a constant pressure. This can be done with a floating piston. We can perform a force balance,

$$P_{gas}A = mg + P_{atm}A,$$

where  $P_{gas}$  is the pressure of the gas,  $A$  is the cross sectional area of the piston,  $m$  is the mass of the piston, and  $P_{atm}$  is the atmospheric pressure.

- **Isochoric:** The process occurs at a constant volume. These occur in rigid vessels. **Rigid vessels** are ones that maintain their shapes during a process.
- **Adiabatic:** The process occurs without heat transfer to or from the system. Adiabatic processes are implied with terms such as **well insulated**. These never occur at a constant temperature.

In thermodynamics, we are concerned with processes that reach a state of equilibrium. In other words, these are processes whose states are independent of time. We will focus on the following types of equilibrium:

- **Mechanical Equilibrium:** The pressure is constant.
- **Thermal Equilibrium:** The temperature is constant.
- **Phase Equilibrium:** There is no tendency for the mass of phases to change.
- **Chemical Equilibrium:** Forward and reverse reactions occur at the same rate.

In theory, attaining equilibrium requires infinite time. However, if a process only deviates from equilibrium by a small amount, we say that we have a **quasi-equilibrium state**. For the sake of our analyses, we will take this to be the **equilibrium state**.

## §4 July 12, 2017

### §4.1 Gibb's Phase Rule

We recall **Gibb's Phase Rule**,

$$F = C - P + 2,$$

where  $F$  is the degrees of freedom,  $C$  is the number of components, and  $P$  is the number of phases in thermodynamic equilibrium with each other. We can have multiple liquid and solid phases, but only one gas phase. The degrees of freedom indicate the number of intensive properties that can be specified independently. The phase rule can be used to determine whether enough information has been given to solve a problem.

### §4.2 Temperature

Sensory perception is an unreliable means of measuring temperature. **Temperature** is formally introduced using the **Zeroth Law of Thermodynamics**. If we replace a body in thermal equilibrium with another, with a device whose properties can be correlated with temperature, we obtain a reliable means of measuring temperature.

### §4.3 Pressure

We define **pressure** as the force normal to the surface divided by the area of the surface,

$$P = \frac{F}{A}.$$

The most common units for pressure are:

- **Pascal (Pa)**:  $1Pa = 1N/m^2$ .
- **bar (bar)**:  $1bar = 10^5Pa$ .
- **atmosphere (atm)**:  $1atm = 101.325kPa$ .
- **Pounds per Square Inch (psi)**:  $psia$  is absolute pressure (gauge and atmosphere), while  $psig$  is gauge pressure. We should only use psi for relative pressure  $\Delta P$ .  $14.696psia = 1atm$ .

In measuring pressure, it simplifies the instrument design if we can neglect atmospheric pressure since it varies with location. We can then define gauge pressure as the absolute pressure minus the atmospheric pressure. In this course, all pressures will be absolute unless specified otherwise.

Any property that changes with respect to pressure can be correlated with pressure. At the bottom of a liquid column of height  $h$ , the pressure is given by  $P_{bottom} = \rho gh$ . If the pressure at the top of the column is non-zero, then we add the pressure at the top of the column to obtain  $P_{bottom} = P_{top} + \rho gh$ . To use a manometer to measure pressure, we note that the side that pushes further the liquid inside has the higher pressure. We can use  $\rho gh$  to determine the pressure differential where  $h$  is the difference in the height of the liquid on either side of the **U-tube manometer**.

#### Example 4.1

Calculate the height of water such that the pressure difference is  $100kPa$ , given that  $g = 9.81m/s^2$  and  $\rho = 10^3kg/m^3$ .

We find that the height is  $10.19m$ .

#### Example 4.2

A manometer is attached to a tank of gas with a pressure greater than atmospheric pressure at  $93kPa$ . The manometer fluid is mercury, with a density of  $\rho = 13.59g/cm^3$ . The height difference across the manometer is  $2cm$ . Determine the gauge pressure and the absolute pressure.

We recall that  $h$  is the height difference within the manometer. First, the gauge pressure is the reading of the manometer. The absolute pressure is obtained by adding the atmospheric pressure to the gauge pressure. With a height difference of  $2cm$ , we find that the gauge pressure is given by

$$P_{gauge} = \rho g(h_3 - h_2) = (13590)(9.81)(.02) = 2666Pa.$$

Therefore, the absolute pressure is given by

$$P = P_{atm} + P_{gauge} = 93000 + 2666 = 95666Pa.$$

Because of the insignificance of gas density, the gas contribution (calculated using the density of gas, the acceleration due to gravity, and the change in height) is often neglected. Note also that the height used to calculate pressure is always the vertical height, even in problems with inclined manometers. When there is more than one fluid in a manometer, we denote the interface pressure as  $P_{int}$ . We can then sum the contributions of the different fluids to determine the overall pressure.

## §5 July 14, 2017

### §5.1 Energy

The **First Law of Thermodynamics** is the conservation of energy equation. This states that the energy change within a system is equal to the net energy transferred across the system boundary. This is given by

$$\Delta E_{universe} = \Delta E_{system} + \Delta E_{surroundings} = 0,$$

where  $\Delta E_{system}$  is the energy change of the system,  $\Delta E_{surroundings}$  is the energy change of the system, and the universe is the system with the surroundings.

The energy of the system and surroundings may change in a variety of ways. **Stored energy** refers to the energy change within the system:

- **Kinetic Energy:** This is the energy due to motion, relative to a particular member. For specific kinetic energy, we divide by mass.
- **Potential Energy:** This is the energy due to a relative position. For specific potential energy, we divide by mass.
- **Internal Energy:** This is the summation of all of the molecule-scaled energies. This is caused by translations, rotations, and vibrations. Internal energy can be found from tabulated data, or from invoking the **Ideal Gas Law**. We use  $U$  to denote the extensive internal energy, and  $u$  to denote the specific internal energy.

Given the preceding cases of stored energy, the energy change of the system is

$$\Delta E_{system} = \Delta KE + \Delta PE + \Delta U.$$

## §5.2 Energy Transfer Across the System Boundary

Energy transfer across a system boundary can occur via heat and work. Heat transfer is energy that is exchanged due to a temperature difference across a system boundary. Energy that flows across a system boundary by means other than a temperature difference is called work. By convention, work is positive when it is done by the system on the surroundings.

### Example 5.1

Examples of positive work done by the system on the surroundings include car engines and plane turbines. Examples of negative work done by the surroundings on the system include compressors and battery charging.

Heat transfer on the other hand, is positive when it is directed into the system. Heat always flows from a higher temperature to a lower temperature. Heat and work are collectively referred to as **transitory energy**, as opposed to stored energy. Heat and work cannot be stored, and can only be defined at the system boundary. The net energy transferred across the system boundary is

$$\Delta E_{\text{boundary}} = -\Delta E_{\text{surroundings}} = Q - W.$$

Therefore, the first law can be stated for a closed system, where

$$Q - W = \Delta KE + \Delta PE + \Delta U.$$

## §5.3 Modes of Heat Transfer

There are three primary ways that heat could transfer:

1. **Conduction:** Heat transfer between two stationary objects which are in perfect contact with each other is conductive. Conductive heat transfer is computed using **Fourier's Law**,

$$Q = -kA \frac{dT(x)}{dx},$$

where  $Q$  is the heat flow in  $W$ ,  $k$  is the thermal conductivity in  $W/m \cdot K$ ,  $A$  is the area normal to the heat flow in  $m^2$ ,  $x$  is the distance in  $m$ . and  $T$  is the temperature in  $K$ . The negative sign arises because heat flows from a higher temperature to a lower temperature.

2. **Convection:** Convective heat transfer arises due to fluid motion. It is computed using **Newton's Law of Cooling**,

$$Q = hA\Delta T,$$

where  $h$  is the convective heat transfer coefficient in  $W/m^2K$ ,  $A$  is the surface area exposed between for heat exchange in  $m^2$ , and  $\Delta T$  is the change in temperature in  $K$ .

3. **Radiation:** Radiative heat transfer is due to electromagnetic energy. The rate of heat transfer is proportional to  $T^4$ .

## §6 July 17, 2017

### §6.1 Work at a Moving Boundary

There are different modes of work: There are different modes of work. This could take the form of a horizontal piston in which a pressure of  $P_{gas}$  pushes the piston a distance of  $x$ . Since the movement is in the direction of force, we have

$$W = \int_{x_1}^{x_2} F_{gas} dx = \int_{x_1}^{x_2} P_{gas} A dx = \int_{V_1}^{V_2} P_{gas} dV,$$

where  $V$  is the extensive volume in  $m^3$ . However, we need a relationship between  $P$  and  $V$  to calculate  $W$ .

- Isochoric System:  $V$  is constant, so  $dV = 0$ . Therefore,

$$W = \int_{V_1}^{V_2} P dV = 0.$$

- Isobaric System:  $P$  is constant. Therefore,

$$W = \int_{V_1}^{V_2} P dV = P \int_{V_1}^{V_2} dV = P \Delta V.$$

- Polytropic Process:  $PV^n = C$ , where  $n$  is an empirical (experimentally derived) constant, and  $C$  is a constant. This is the process path imposed by external forces. It is independent of any equation of state (such as the ideal gas law). When one has experimental data for  $P$  versus  $V$ , the value of  $n$  can be found by plotting,

$$\ln(P) = -n \ln(V) + \ln(C).$$

Therefore, we can derive an expression for work,

$$W = \int_{V_1}^{V_2} P dV = \int_{V_1}^{V_2} \frac{C}{V^n} dV = \frac{1}{1-n} (P_2 V_2 - P_1 V_1).$$

This is valid for all fluids. For an ideal gas, we have  $PV = mRT$ , where  $R$  is the gas constant such that the molecular weight multiplied by  $R$  equals the universal gas constant  $R_u$ . Thus, only for ideal gases in a closed system, this can be expressed as,

$$W = \frac{mR}{1-n} (T_2 - T_1).$$

In this course,  $R$  is the specific gas constant with units  $J/kgK$ . The universal gas constant  $R_u$  has units  $J/molK$ .

## §7 July 19, 2017

### §7.1 Work Examples

**Example 7.1**

The pressure in a  $0.2m^3$  cylinder of propane at  $300K$  is  $100kPa$ . At  $240K$ , determine the mass of the propane in the cylinder, the final pressure, the final volume, and the work during this process.  $PV^{1.1}$  is constant.

*Solution.* Since  $PV^{1.1}$  is constant, this implies that  $n = 1.1$ . To find the mass of propane, we will assume that propane is an ideal gas, so  $m = PV/RT$ . Thus,

$$\frac{P_1 V_1}{RT_1} = \frac{P_2 V_2}{RT_2},$$

since  $m_1 = m_2$ . This equation relates the pressure and volume within the fluid.  $PV^{1.1} = C$  is external upon the fluid. This is how the system goes from the first state to the second state. For an ideal gas undergoing a polytropic process, recall that  $W = (P_2 V_2 - P_1 V_1)/(n - 1)$ . Also recall the first law of thermodynamics, which states that  $Q - W = \Delta KE + \Delta PE + \Delta U$ . This gives us

$$m = \frac{P_1 V_1}{RT_1} = \frac{(100 \cdot 10^3 Pa)(0.2m^2)}{(188.5J/kg)(300K)} = 0.3537kg.$$

To find  $P_2$ , it is known that  $P_1 V_1^{1.1} = P_2 V_2^{1.1}$ . From the ideal gas law, we can equate  $P_1 V_1/T_1$  with the values for pressure, volume, and temperature at the second state. Thus, we obtain

$$\begin{aligned} \frac{T_2}{T_1} &= \left( \frac{P_2}{P_1} \right)^{1-\frac{1}{n}}, \\ \frac{V_2}{V_1} &= \left( \frac{T_2}{T_1} \right)^{\frac{1}{1-n}}. \end{aligned}$$

Solving the first equation for  $P_2$ , we find that

$$P_2 = P_1 \left( \frac{T_2}{T_1} \right)^{\frac{n}{n-1}} = (100kPa) \left( \frac{340K}{300K} \right)^{\frac{1.1}{0.1}} = 396kPa.$$

To find  $V_2$ , we apply the second equation to find that

$$V_2 = V_1 \left( \frac{T_2}{T_1} \right)^{\frac{1}{1-n}} = (0.2m^2) \left( \frac{340}{300} \right)^{-10} = 0.0572m^3.$$

Finding the work done, we use the equation for polyprotic processes,

$$\begin{aligned} W &= \frac{1}{1-n} (P_2 V_2 - P_1 V_1) \\ &= \frac{1}{1-1.1} ((396 \cdot 10^3 Pa)(0.0572m^3) - (100 \cdot 10^3 Pa)(0.2m^3)) \\ &= -2.67kJ. \end{aligned}$$

■

**Remark 7.2.** For a polyprotic process, we can use the above expression for work when the fluid is an ideal gas and  $n \neq 1$ . If  $n$  where unity, then  $PV = C$  for a constant  $C$ . For an ideal gas, we can still find an expression for the work. If  $PV = mRT$  is a constant, then the process must be isothermal, Thus, for an ideal gas undergoing an isothermal process,

$$W = \int_{V_1}^{V_2} P dV = mRT \int_{V_1}^{V_2} \frac{dV}{V} = mnRT \frac{V_2}{V_1},$$

where  $n = 1$  in an ideal gas.



## §7.2 Types of Processes

When the process is isobaric (constant  $P$ ),  $n = 0$ . When the process is isothermic (constant  $T$ ), then  $n = 1$ . Otherwise, when the process is adiabatic ( $Q = 0$ ), then  $n = 1 - \gamma$ .

## §8 July 28, 2017

### §8.1 Property Table Examples

To determine which property table to use for a given problem, we first need to compare with the saturation conditions.

#### Example 8.1

Determine the number of phases that are present when water is at  $1.5\text{MPa}$  and  $600^\circ\text{C}$ .

*Solution.* Consulting the *Table A-5, Saturated water - Pressure table*, the saturation temperature at  $1500\text{kPa}$  is found to be  $198.29^\circ\text{C}$ . Thus, at  $600^\circ\text{C}$ , we have a temperature that is greater than the saturated temperature. Therefore, we have a superheated vapour. ■

#### Example 8.2

Determine the phases that are present when water is at  $1.5\text{MPa}$  and  $20^\circ\text{C}$ .

*Solution.* Since we are below the saturation temperature at  $1.5\text{MPa}$ , we have a compressed liquid. ■

#### Example 8.3

Determine the phases that are present when  $P = 1.5\text{MPa}$  and quality  $x = 0.6$ .

*Solution.* Quality is only defined when we are in the two phase region. Thus, we have vapour and liquid. ■

#### Example 8.4

Determine the number and type of phases present at  $P = 1.5\text{MPa}$  and  $h = 2300\text{kJ/kg}$ .

*Solution.* Consulting *Table A-5* for enthalpy, we note that the given value of  $h$  is between the  $h_f$  of the saturated liquid ( $844.55\text{kJ/kg}$ ) and  $h_g$  of the saturated vapour ( $2791.0\text{kJ/kg}$ ). Thus, we are again in the two phase region. Since  $h_f < h < h_g$ , we have a saturated liquid in equilibrium with a saturated vapour. We can calculate the quality,

$$x = \frac{h - h_f}{h_g - h_f} = \frac{2300 - 844.55}{2791 - 844.55} = 0.748.$$

■

**Remark 8.5.** To find quality, we can use specific volume, internal energy, enthalpy, or entropy values. In the above example, we used the enthalpy values  $h$ . If we want to find the enthalpy value below that of the saturated liquid  $h_f$ , we can determine the temperature from the pressure, then consult *Table A-4*. We can then linearly interpolate for the saturation temperature in order to determine  $h$ .

#### Example 8.6

A rigid tank contain  $50\text{kg}$  of water at  $90^\circ\text{C}$ . If the water is known to be a saturated liquid, determine the volume that it occupied.

*Solution.* We will assume that the tank is completely full of water. Since we have a saturated liquid at a given temperature, we use *Table A-4*. The volume is therefore the specific volume multiplied by the mass, so

$$V = v \cdot m = (0.001036\text{m}^3/\text{kg}) (50\text{kg}) = 0.0518\text{m}^3.$$

The pressure of  $70.183\text{kPa}$  (saturation pressure) in the tank can be determined by consulting *Table A-4* for water at  $90^\circ\text{C}$ . ■

#### Example 8.7

Determine the volume that water occupied when  $P = 4\text{MPa}$ ,  $T = 420^\circ\text{C}$ , and  $m = 2\text{kg}$ .

*Solution.* Consulting *Table A-5* at the specified pressure, we note that our temperature is greater than the saturation temperature. Thus, we have superheated water. We can then perform a linear interpolation on the entries of *Table A-6* to find the specific volume of the superheated water. Then, we can use the given mass to find the total volume. ■

#### Example 8.8

Determine the specific volume of water at  $0.18\text{MPa}$  and  $170^\circ\text{C}$ .

*Solution.* Consulting *Table A-4*, since the pressure is less than the saturation pressure, we are in the superheated vapour region. We now consult *Table A-6*. We have tables at  $P = 0.1\text{MPa}$  and  $P = 0.2\text{MPa}$ . We will now linearly interpolate between these two tables between  $T = 150^\circ\text{C}$  and  $T = 200^\circ\text{C}$  to find the specific volume  $v$  at  $170^\circ\text{C}$  at these two pressures. We then interpolate for our pressure of  $0.18\text{MPa}$ . ■

#### Example 8.9

Consider a rigid tank containing  $10\text{kg}$  of water at  $90^\circ\text{C}$ . If  $8\text{kg}$  of water is in the liquid phase, determine the pressure in the tank and the volume of the tank.

*Solution.* Since there are two phases (vapour and liquid) present,  $P = P_{\text{sat}} = 79.184\text{kPa}$  according to *Table A-4*. To determine the volume of the tank, we first note that

$$x = \frac{M_g}{M_t} = \frac{M_t - M_f}{M_t} = \frac{10 - 8}{10} = 0.2.$$

Thus, by using *Table A-4*(9?), the total tank volume can be determined,

$$V = m_f v_f + m_g v_g = (8\text{kg}) (0.001036\text{m}^3/\text{kg}) + (2\text{kg}) (2.3593\text{m}^3/\text{kg}) = 4.73\text{m}^3.$$

■

**Remark 8.10.** The mass fraction and volume fractions are generally different.

## §9 July 31, 2017

### §9.1 Property Table Examples Cont'd

#### Example 9.1

A two-phase liquid-vapour mixture of water has a temperature of  $300^\circ\text{C}$  and a quality of  $x = 75\%$ . The mixture occupies a volume of  $0.05\text{m}^3$ . Determine the mass of the saturated liquid and the mass of the saturated vapour.

*Solution.* From *Table A-4*,  $P = P_{\text{sat}} = 8587.9\text{kPa}$ ,  $v_g = 0.021659\text{m}^3/\text{kg}$ , and  $v_f = 0.001404\text{m}^3/\text{kg}$ . Recall that  $v_{\text{total}} = m_t v_{\text{ave}}$ . Now, we can find the average volume as,

$$\begin{aligned} v_{\text{ave}} &= v_f + x(v_g - v_f) \\ &= 0.001404\text{m}^3/\text{kg} + 0.75 (0.021659\text{m}^3/\text{kg} - 0.001404\text{m}^3/\text{kg}) \\ &= 0.016595\text{m}^3/\text{kg} \end{aligned}$$

Since the total volume of the two-phase mixture is given, the total mass can be found,

$$m = \frac{v}{v_{\text{ave}}} = \frac{0.05\text{m}^3}{0.016595\text{m}^3/\text{kg}} = 3.0129\text{kg}.$$

Therefore,

$$\begin{aligned} m_g &= x m_t = 0.75(3.0129\text{kg}) = 2.2596\text{kg}, \\ m_f &= m_t - m_g = 3.0129\text{kg} - 2.2596\text{kg} = 0.7532\text{kg}. \end{aligned}$$

■

### §9.2 Thermodynamic Properties of an Ideal Gas

Recall that the first law of thermodynamics for a **closed system** states that,

$$Q - W = \Delta KE + \Delta PE + \Delta U.$$

In using this equation, we have seen that  $W$  and  $\Delta U$  depend on the fluid properties. For water and R-134a, property tables are available for looking up  $v$ ,  $u$ ,  $h$ , and the other thermodynamic properties.

For an ideal gas however, the necessary connection for finding  $\Delta u$  for an ideal gas is the specific heat capacity. The **specific heat capacity** is usually defined as the amount of energy in  $\text{kJ}$  needed to raise the temperature of  $1\text{kg}$  of a substance by  $1\text{K}$ . However, this definition is incomplete because heat, like work, depends upon the path of a process.

- For a **constant volume** process (assuming  $\Delta KE = \Delta PE = 0$ ), the work term cancels out since  $W = \int P \Delta V = 0$ . Therefore, the expression becomes,

$$Q = \Delta U = m \Delta u.$$

- For a **constant pressure** process, the work term becomes  $W = P\Delta V$ . Thus, the expression becomes,

$$Q = \Delta U + P\Delta V.$$

This can also be expressed as

$$Q = m(\Delta u + P\Delta v) = m\Delta h,$$

where  $h$  is the specific enthalpy.

Specific heat can therefore be defined under constant volume or constant pressure. The units are  $kJ/kgK$ .

$$C_V = \left( \frac{\partial u}{\partial T} \right)_v,$$

$$C_P = \left( \frac{\partial h}{\partial T} \right)_p.$$

Because  $C_V$  and  $C_P$  are primarily functions of temperature, we often replace the partial derivatives with ordinary derivatives. As a consequence, we find that for ideal gases,

$$\Delta u = \int_{T_1}^{T_2} C_V dT = C_V \Delta T,$$

$$\Delta h = \int_{T_1}^{T_2} C_P dT = C_P \Delta T.$$

For an ideal gas, it can be shown that

$$\begin{aligned} h &= u + Pv \\ &= u + RT \\ dh &= du + RdT \\ C_p dT &= C_v dT + RdT \\ C_p &= C_v + R \end{aligned}$$

## §10 August 2, 2017

### §10.1 Specific Heat Capacity

Assuming that  $C_P$  is constant, it can be found that

$$\begin{aligned} \Delta u &= (C_P - R)(T_2 - T_1), \\ \Delta h &= C_P(T_2 - T_1). \end{aligned}$$

When a functional form of  $C_P = f(T)$  is tabulated, one typically finds a polynomial correlation with one of the following forms:

- **Molar Specific Heat** in  $kJ/molK$  is given by  $\overline{C_P} = a + bT + cT^2 + dT^3$ . See Table A-2.
- **Molar Specific Heat** in  $kJ/molK$  is also given by  $\overline{C_P} = a + bT + cT^2 + d/T^3$ . This is less common.

The constant  $a, b, c, d$  are only valid for a specific range. Avoid extrapolating with one of these polynomials. One source for comprehensive  $C_P$  data is the NIST (National Institute of Standards) database.

**Example 10.1**

1kg of air at  $100^\circ\text{C}$  and  $88\text{kPa}$  occupies one chamber of a vessel whose other chamber is initially evacuated. Each chamber has a volume of  $1\text{L}$ . Once the partition is removed, heat is transferred between the vessel and surroundings such that the final temperature is  $5^\circ\text{C}$ . Find  $Q$ .

*Solution.* We will first draw the system boundary of the initial state and final state. Doing so, we obtain a closed system. Note that in thermodynamics, we are only concerned with the final and initial states. Thus, the mechanism by which the partition is removed is not relevant. Since this is a closed system, mass stays constant. Assuming ideal gas behaviour, we can apply

$$\frac{P_1 V_1}{RT_1} = \frac{P_2 V_2}{RT_2}.$$

Additionally, with no work term, we can apply the first law to obtain

$$\begin{aligned} Q &= \Delta U \\ &= m\Delta u \\ &= m \int_{T_1}^{T_2} C_V dT \\ &= \frac{m}{MW} \int_{T_1}^{T_2} \overline{C_V} dT \\ &= \frac{m}{MW} \int_{T_1}^{T_2} (\overline{C_p} - R_u) dT \\ &= \frac{m}{MW} \int_{T_1}^{T_2} ((a - Ru) + bT + cT^2 + dT^3) dT \\ &= \frac{m}{MW} \left[ (a - R_u)T + \frac{bT^2}{2} + \frac{cT^3}{3} + \frac{dT^4}{4} \right]_{T_1}^{T_2} \end{aligned}$$

Substituting  $T_1 = 278.15\text{K}$  and  $T_2 = 373.15\text{K}$ , we obtain

$$Q = -68.47\text{kJ},$$

resulting in heat being removed from the system. ■

We would like to be able to determine  $u$  or  $h$  for an ideal gas. We will need to choose an arbitrary reference state for which  $u_{ref} = 0$ . Let us say that  $u_{ref} = 0$  at  $T_{ref} = 0\text{K}$  for an ideal gas. The associate  $h_{ref}$  value is therefore given as  $h_{ref} = u_{ref} + (Pv)_{ref}$ . For an ideal gas,  $Pv = RT$ , so  $h_{ref} = (RT)_{ref} = 0$ . Therefore,

$$\Delta u = \int_{T_{ref}}^T C_V dT,$$

$$\Delta h = \int_0^T C_P dT.$$

If  $C_P$  and  $C_V$  are constant between 0 and  $T$ , then for ideal gases, we have

$$u(T) = C_V T = (C_P - R)T,$$

$$h(T) = C_P T.$$

Alternatively,  $u(T)$  and  $h(T)$  are tabulated for many ideal gases.

## §10.2 Real Fluid Problems

The specific volume of a real gas can be found from an equation of state, or from generalized correlations. There are many equations of state. Each equation of state is tailored to specific systems of compounds. An equation of state that is geared towards light hydrocarbons will not suffice when applied to something like alcohols. Generalization correlation (the principle of corresponding states) is given by

$$PV = ZmRT,$$

where  $Z$  is the compressibility factor for a real fluid. In the compressibility chart for  $Z$ , this is correlated with reduced pressure and reduced temperature.

## §11 August 4, 2017

### §11.1 First Law for Closed Systems

#### Example 11.1

A  $3m^3$  rigid tank contains  $H_2$  at  $250kPa$  and  $550K$ . The tank is subsequently cooled until the temperature is  $350K$ . Find the mass of  $H_2$  in the tank, the final pressure in the tank, the work done during the process, and the amount of heat transferred to or from the tank.

*Solution.* We will assume that  $H_2$  is an ideal gas with a constant  $C_V$  of  $10.377kJ/kgK$  (This is the average  $C_V$  taken from *Table A-2B* at the average system temperature of  $(350K + 550K)/2 = 450K$ . The system boundary is the volume that contains all of the  $H_2$  inside the rigid tank. This is a closed system where  $V$  is constant, so  $dV = 0$ . Because this is a closed system, ideal gas behaviour is assumed, and the first law of thermodynamics is applied without movement (resulting in changing kinetic and potential energy),

$$\begin{aligned} m_1 &= m_2, \\ \frac{P_1 V_1}{RT_1} &= \frac{P_2 V_2}{RT_2} \implies \frac{P_1}{T_1} = \frac{P_2}{T_2}, \\ Q - W &= \Delta U. \end{aligned}$$

By the first law, since there is no movement for change in kinetic or potential energy, To find the mass, we use *Table A-1* to find the specific gas constant of  $H_2$ , and then apply the ideal gas law,

$$m = \frac{P_1 V_1}{RT_1} = \frac{250kPa (3m^3)}{4.124kJ/kgK(550K)} = 0.3307kg.$$

Applying the second relation,  $P_2$  can be solved,

$$P_2 = P_1 \left( \frac{T_2}{T_1} \right) = 250kPa \left( \frac{350K}{550K} \right) = 159.1kPa.$$

The work can be determined by integrating pressure multiplied by the differential volume, where  $W = \int PdV$ . However, we recall that  $dV = 0$  since this is an isochoric process. Thus,  $W = 0$ .

To determine the heat transferred, we apply the third relation above (the first law of thermodynamics) to find that

$$Q = \Delta U = mC_V(T_2 - T_1) = (0.3307kg)(10.377kJ/kgK)(350K - 550K) = -686.3kJ.$$

Thus, heat is removed from the system. ■

**Example 11.2**

A  $0.5\text{m}^3$  rigid tank contains saturated water vapour (steam) at  $150^\circ\text{C}$ . The tank is cooled until the quality of the water is 50%. Sketch a well labelled  $T - v$  diagram of the process. Then, find the mass of water in the tank in the initial state, and the final temperature.

*Solution.* The system boundary is defined as the volume that encloses the  $\text{H}_2\text{O}$  in the rigid tank. We also have a closed system with a constant  $V$ . Note that  $\text{H}_2\text{O}$  cannot be assumed ideal (due to the polar nature of water molecules). Thus, property tables are used. Since this is a closed system,

$$m_1 = m_2,$$

$$v_1 = v_{2,ave},$$

where  $m$  is the mass and  $v$  is the specific volume. Here,  $v_{2,ave}$  denotes the average specific volume of the mixture of liquid water and water vapour.

To draw the  $T - v$  diagram, we note that we start at a point on the right edge where we have saturated water vapour at  $T = 150^\circ\text{C}$ . Since the tank is then cooled, we move downwards until the left and right portions are equal (since quality is 0.5). This occurs at a certain temperature  $T_2$ , which is to be determined.

From Table A-4, we know that the specific volume of water as a saturated vapour at  $150^\circ\text{C}$  is  $0.39248\text{m}^3/\text{kg}$ . Thus, the mass in the initial state can be determined as,

$$m = \frac{V}{v_1} = \frac{0.5\text{m}^3}{0.39248\text{m}^3/\text{kg}} = 1.2748\text{kg}.$$

To determine the final temperature  $T_2$ , we recall that  $v_{2,ave} = v_1$ , where

$$v_{2,ave} = xv_g + (1 - x)v_f = 0.5v_g + 0.5v_f.$$

Now, we note that at  $T = 150^\circ\text{C}$ ,  $v_g \gg v_f$  and thus  $v_{2,ave} \gg v_f$ . Therefore,  $x \approx v_{2,ave}/v_g$ . Since we know  $x$  and  $v_{ave}$ ,

$$v_g \approx \frac{v_{2,ave}}{x} \approx \frac{0.39248\text{m}^3/\text{kg}}{0.5} \approx 0.785\text{m}^3/\text{kg}.$$

Table A-4 indicates that  $T_2$  lies between  $120^\circ\text{C}$  and  $125^\circ\text{C}$ . We will now use  $v = 0.5$  to compute  $v$  at  $120^\circ\text{C}$  and  $v$  at  $125^\circ\text{C}$  by linear interpolation,

$$v_{120} = 0.001060\text{m}^3/\text{kg} + 0.5(0.89133\text{m}^3/\text{kg} - 0.001060\text{m}^3/\text{kg}) = 0.4462\text{m}^3/\text{kg},$$

$$v_{125} = 0.001065\text{m}^3/\text{kg} + 0.5(0.77012\text{m}^3/\text{kg} - 0.001065\text{m}^3/\text{kg}) = 0.3856\text{m}^3/\text{kg}.$$

Now, linearly interpolating the temperature for the actual  $v_{2,ave} = 0.39248\text{m}^3/\text{kg}$  when  $v_{120} = 0.4462\text{m}^3/\text{kg}$  at  $120^\circ\text{C}$  and  $v_{125} = 0.3856\text{m}^3/\text{kg}$  at  $125^\circ\text{C}$ , we find that  $T_2 = 124.4^\circ\text{C}$ . ■

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