

# 1 CHE 205: THERMODYNAMICS

## 2 Introduction

3 The words “thermo” and “dynamics” are of Greek origin meaning heat and work respectively.  
4 Therefore, thermodynamics is the study of the transformations or relationships between heat and  
5 work with respect to a particular system. Considering that both heat and work are forms of energy,  
6 therefore, thermodynamics can be defined as the study of energy transformations.

7 Thermodynamics is a macroscopic study that is based on the bulk properties of matter. That is, it  
8 considers the large scale properties of matter. It does not provide information at the molecular  
9 level. Statistical thermodynamics study energy transformations at the molecular levels.

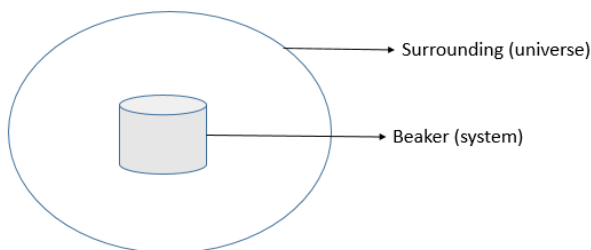
10 Information about the thermodynamic properties of reactants and products can help us to determine  
11 which direction a reaction will proceed; whether spontaneous or not. However, thermodynamics  
12 does not give information about how fast a reaction will proceed.

### 13 *Definition of thermodynamic terms*

14 A number of terms are commonly used in thermodynamic studies and it is important to define  
15 them before proceeding.

16 **1. System:** A system is that part of the universe that is currently been studied. For example a  
17 reaction occurring in a beaker in the laboratory

18 **2. Surroundings:** the surroundings constitute every other part of the universe outside of the system  
19 been studied. For instance, in a reaction taking place in a beaker, the beaker and its content are the  
20 system while the entire universe is the surrounding.



21

22 Therefore, the combination of the system and the surrounding makes the universe.

## *Types of systems*

In terms of transfer of matter and energy between a system and its surroundings, a system can be classified as”

1. **Open system:** This is a system where there is **transfer of matter and energy** between the system and its surroundings.
2. **Closed system:** In this system, there is a **transfer of energy, but not matter**, between a system and its surrounding. E.g. A beaker of water in a thermostated water bath can receive energy from the hot water bath but there is no transfer of matter (water) between the beaker and the bath.
3. **Isolated system:** This is a system where **neither energy nor matter is transferred** between the system and its surrounding.

## *Thermodynamic properties*

The properties of thermodynamic systems can be broadly classified into extensive and intensive properties.

- (i) **Extensive properties** are those properties whose value are **dependent on the amount or size** of the substance present in the system. E.g. mass, volume, heat capacity, internal energy, entropy. The overall value is the sum of the various parts of the system.
- (ii) **Intensive properties** are properties that **do not depend on the size or amount** of substance in the system. E.g. temperature, pressure, surface tension, viscosity, density. The temperature of a particular body of water is expected to be the same regardless of the amount of the water that was tested with a thermometer.

## **State of a system: State variables and state functions**

Thermodynamic systems are described by certain measurable bulk properties. These are called **thermodynamic variables or state variables**. They include: pressure, volume, temperature and composition. Note that a system can have other properties like density, refractive index, viscosity e.t.c. The main properties that describes a system are the state variables (P,V,T and n). The state

variables can influence other properties of the system. At fixed values of state variables, other properties are fixed. For instance, at 1 atm and 103°C, the state of water will be gaseous. The state will be maintained as long as this values are maintained.

*State functions* are the properties of a system on which the state of a system depends and their **values does not depend on the path** through which the value was obtained. That is, the change in the value depends on the initial and final state, the means of obtaining the change does not matter. Examples of state functions are temperature, pressure, volume, internal energy.

### **Internal energy as a state function**

Internal energy (E) is the sum total of all the energy present in a system by virtue of its molecular constitution and motion of its molecules. We cannot measure the absolute value of E at a particular state. What we measure is the change in internal energy ( $\Delta E$ ). It is a state function because it does not depend on the path followed to achieve the change. It only depends on the initial and final states of the system. Internal energy can be changed when:

1. Work is done on the system (+w) or by the system (-w)
2. Heat is transferred to the system (+q) or from the system (-q)
3. Matter is transferred to the system or from the system.

The change in internal energy of a system can be expressed in terms of heat exchange (q) and work done on or by the system as

$$\Delta E = q + w$$

The above equation is the statement of the first law of thermodynamics.

### **Laws of thermodynamics**

There are four laws upon which the study of classical thermodynamics stands. They are the zeroth law, first law, second law and third laws of thermodynamics.

#### ***Zeroth law of thermodynamics***

The law states that if two bodies are each in thermal equilibrium with a third body, then they are also in thermal equilibrium with each other. That is, if a body, A, is in thermal equilibrium, C, (A=C), and body, B, is in equilibrium with C (B=C), then A and B are in equilibrium.

### ***First law of thermodynamics***

This law states that energy can neither be created nor destroyed, but it can be converted from one form to another. This is also known as the law of conservation of energy. On a larger scale, this law implies that the energy of the universe is constant.

### ***Second law of thermodynamics***

The law states that the entropy of an isolated system always increases. An example of this is when heat flows from a hot body to a cold body. A natural process or a spontaneous process will occur in the direction of increase in entropy.

### ***Third law of thermodynamics***

This law states that the entropy of a system at absolute zero is zero.

There are practical applications of these laws as we shall discuss subsequently

## **APPLICATION OF THE FIRST LAW OF THERMODYNAMICS**

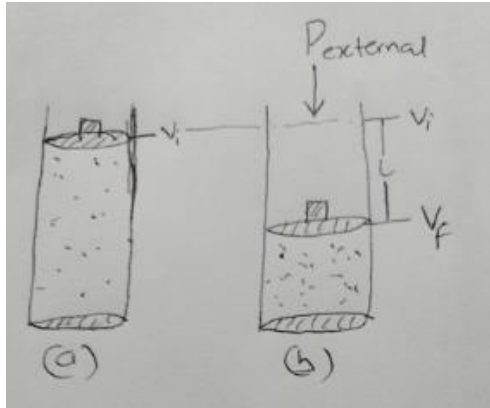
The first law of thermodynamics states that energy is always conserved. In other words, the internal energy of a system changes when energy in terms of heat is transferred to or from the system and work is done by or on the system.

Mathematically, the first law is represented as

$$\Delta E = q + w$$

### **1. Work**

Consider one mole of an ideal gas in a container closed with a frictionless piston. If an external pressure was applied to compress the gas from an initial volume,  $V_i$ , (fig a) to another volume,  $V_f$ , (fig b), the change in volume  $\Delta V = V_f - V_i$ . The piston has moved a distance of  $l$ .



101

102 Therefore, work done by the piston on the system is:

103

$$\text{Work} = \text{force} \times \text{distance} = F \times l$$

104

$$\text{But pressure, } P = \frac{F}{A}. \text{ Therefore, } F = P_{\text{ext}} \times A$$

105

$$\text{Work} = F \times l = P_{\text{ext}} \times A \times l$$

106

$$\text{Volume, } V, = A \times l$$

107

$$\text{Therefore, Work} = P_{\text{ext}} \Delta V$$

108

Since  $V_f < V_i$ ,  $\Delta V$  will be negative. Since work was done on the system,  $W$  has to be +ve. In

109

order to neutralize the negative sign of  $\Delta V$ , a negative sign has to be introduced to  $W$ .

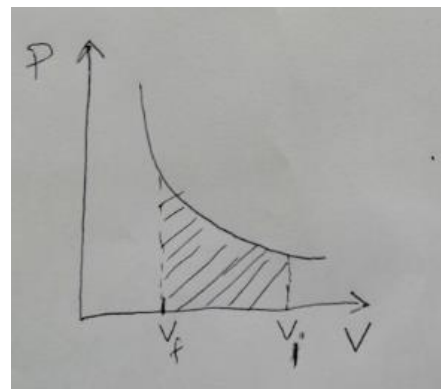
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$$\text{Therefore, Work} = - P_{\text{ext}} \Delta V$$

111

Using the P-V diagram below, the work done,  $P(-\Delta V)$  can be integrated as the area of the shaded

112



113

114

115

$$W = -P \int_{V_i}^{V_f} \Delta V$$

116 The expression  $\Delta E = q - W$  is more commonly used

117

## 118 2. Enthalpy (H)

119 Enthalpy is the heat content of a system. It is a state function whose value does not depend on the  
120 path. Mathematically, enthalpy is given as:

121

$$H = E + PV$$

122 It is the sum of the internal energy (E) and work given as the product of pressure and volume.

123 NOTE the terminologies below:

124 A process that occur at constant pressure is called **isobaric**. i.e.  $\Delta P=0$ .

125 A process that occur at constant volume is called **isometric**. i.e.  $\Delta V=0$ .

126 A process that occur at constant temperature is called **isothermal**. i.e.  $\Delta T=0$ .

127 A process where there is no exchange of heat is called **adiabatic** i.e.  $q=0$

128

### 129 Heat changes at constant volume and constant pressure

#### 130 At constant volume:

131 Recall from the first law that  $\Delta E = q - W$  where  $W = P\Delta V$

132 Therefore,  $\Delta E = q - P\Delta V$

133 At constant volume,  $\Delta V=0$ .

134 Therefore,  $\Delta E = q_v$  (the subscript v indicates at constant volume)

135 This means that the **heat exchange at constant volume is equal to the change in internal**  
136 **energy**.

137 **At constant pressure:**

138 Chemical reactions and biological processes usually take place under constant pressure  
139 (atmospheric pressure).

140 From the first law  $\Delta E = q - P\Delta V$ .

141 At constant pressure,  $q$  is denoted as  $q_p$ .

142 
$$\Delta E = q_p - P\Delta V$$

143 
$$q_p = \Delta E + P\Delta V$$

144 From product rule,  $\Delta (PV) = P\Delta V + V\Delta P$

145 At constant  $P$ ,  $\Delta P = 0$ . Therefore,  $\Delta (PV) = P\Delta V$

146 
$$q_p = \Delta E + \Delta (PV)$$

147 
$$q_p = \Delta(E + PV)$$

148 Recall that enthalpy,  $H$ ,  $= E + PV$

149 Therefore,  $q_p = \Delta H$

150 This means that the **heat exchange at constant pressure is equal to the change in enthalpy**.

151

152 Learning outcomes so far

- 153
- Define thermodynamics terminologies such as system and surroundings; isothermal,
  - 154 isobaric, isometric and adiabatic processes.
  - 155 • Differentiate between open, closed and isolated systems
  - 156 • Understand intensive and extensive properties with examples
  - 157 • State the laws of thermodynamics
  - 158 • Understand the mathematical expression of the first law

- Apply the first law to derive the expressions for heat exchange at constant volume ( $q_v$ ) and at constant pressure ( $q_p$ )

## Heat capacity

The heat capacity of a system is the quantity of heat required to raise a unit mass of the system by  $1^\circ$ . That is, the amount of heat required to effect a  $1^\circ$  rise in temperature. It is an extensive property and has the SI unit of J/K. For a small quantity of heat ( $\delta q$ ) added to the system, the temperature changes by  $\Delta T$ .

Therefore, heat capacity is  $C = \delta q / dT$ .

Heat capacity can be expressed in two forms:

1. Heat capacity at constant pressure ( $C_p$ )
2. Heat capacity at constant volume ( $C_v$ )

From  $C = \delta q / dT$

**At constant pressure:**  $C_p = q_p / dT$ . Recall that  $q_p = \Delta H$ .

Therefore,  $C_p = \Delta H / dT$

**At constant volume:**  $C_v = q_v / dT$ . Recall that  $q_v = \Delta E$

Therefore,  $C_v = \Delta E / dT$

From  $\Delta H = \Delta E + P\Delta V$

Dividing through by  $\Delta T$ ,

$$\frac{\Delta H}{\Delta T} = \frac{\Delta E + P\Delta V}{\Delta T}$$

Substituting  $C_p$  for  $\Delta H / \Delta T$  and  $C_v$  for  $\Delta E / \Delta T$ , we have

$$C_p = C_v + P\Delta V / \Delta T$$



181 For 1 mole of an ideal gas,  $P\Delta V/\Delta T = R$

182 Therefore,  $C_p = C_v + R$  (for one mole of a gas)

183 Or  $C_p = C_v + nR$  (for n moles of a gas)

184

## 185 **Reversible and irreversible processes**

186 A reversible process is a **slow process** where the properties of the system are at equilibrium at  
187 every instance. On the other hand, an irreversible process is a **rapid process** which cannot attain  
188 equilibrium.

189

## 190 **Reversible adiabatic process**

191 An adiabatic process is a process where there is no exchange of heat between a system and its  
192 surrounding. i.e.  $q = 0$ .

193 
$$\Delta E = q - W$$

194 If  $q = 0$ ,  $\Delta E = -W$  ..... (1)

195 
$$\Delta E = -P\Delta V$$

196 Recall,  $C_v = \Delta E/\Delta T$ . Therefore,  $\Delta E = C_v\Delta T$

197 We then have  $C_v\Delta T = -P\Delta V$ .....(2)

198 For one mole of an ideal gas,  $PV = RT$ ,  $P = RT/V$

199 Therefore,  $C_v\Delta T = -\frac{RT}{V}\Delta V$

200 
$$C_v \frac{\Delta T}{T} = -R \frac{\Delta V}{V}$$

201 
$$C_v \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

202 
$$C_v \ln\left(\frac{T_2}{T_1}\right) = -R \ln\left(\frac{V_2}{V_1}\right)$$

$$C_v \ln \left( \frac{T_2}{T_1} \right) = R \ln \left( \frac{V_1}{V_2} \right)$$

$$\ln \left( \frac{T_2}{T_1} \right) = \frac{R}{C_v} \ln \left( \frac{V_1}{V_2} \right)$$

$$\ln \left( \frac{T_2}{T_1} \right) = \ln \left( \frac{V_1}{V_2} \right)^{R/C_v}$$

$$\left( \frac{T_2}{T_1} \right) = \left( \frac{V_1}{V_2} \right)^{R/C_v}$$

$$\text{Since } C_p = C_v + R, \text{ Therefore } \left( \frac{T_2}{T_1} \right) = \left( \frac{V_1}{V_2} \right)^{\frac{C_p - C_v}{C_v}}$$

$$\left( \frac{T_2}{T_1} \right) = \left( \frac{V_1}{V_2} \right)^{\frac{C_p}{C_v} - 1}$$

$$C_p/C_v = \gamma \text{ (heat capacity ratio)}$$

$$\text{Therefore, } \left( \frac{T_2}{T_1} \right) = \left( \frac{V_1}{V_2} \right)^{\gamma - 1}$$

$$T_2 V_2^{\gamma - 1} = T_1 V_1^{\gamma - 1} \dots \dots \dots (3)$$

This is the equation linking **V and T** for reversible adiabatic processes.

The expression can be modified to give a relationship between **P and V** by using the ideal gas equation  $PV = nRT$ .

For one mole of a gas,  $T = PV/R$ . substituting  $P_2 V_2/R$  and  $P_1 V_1/R$  for  $T_2$  and  $T_1$  respectively in equation 3, we have:

$$P_2 V_2^\gamma = P_1 V_1^\gamma \dots \dots \dots (4)$$

Also, the relationship between P and T can be derived from equation 3 by substituting  $V_2 = RT_2/P_2$  and  $V_1 = RT_1/P_1$ . When you play around with the substitution and rearrangement (I suggest you should), we obtain the expression:

$$(P_2/P_1)^{1-\gamma} = (T_1/T_2)^\gamma \dots \dots \dots (5)$$

222 The results of equation 3, 4 and 5 can be summarized as  $TV^{\gamma-1} = \text{constant}$ ;  $PV^{\gamma} = \text{constant}$  and  $T^{\gamma}$   
223  $P^{1-\gamma} = \text{constant}$ .

224 Questions

225 1. Two moles of an ideal gas ( $C_v = 12.5 \text{ J mol}^{-1} \text{ K}^{-1}$ ) at 300 K are **compressed adiabatically** to  $\frac{1}{4}$   
226 of the initial volume. What is the temperature of the gas after compression? Take  $R = 8.3142 \text{ J}$   
227  $\text{mol}^{-1} \text{ K}^{-1}$

228 Solution

229 Given:  $n = 2$ ;  $C_v = 12.5 \text{ J mol}^{-1} \text{ K}^{-1}$ ;  $T_1 = 300 \text{ K}$   $V_2 = V_1/4$

230 From  $C_p = C_v + nR$

231 
$$C_p = 12.5 + 2 (8.314)$$

232 
$$= 29.128 \text{ J mol}^{-1} \text{ K}^{-1}$$

233 
$$\gamma = C_p/C_v = 29.128/12.5 = 2.33024$$

234 This problem is about volume-temperature relationship under adiabatic condition. Therefore, the  
235 right equation is equation 3:

236 
$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

237 
$$\frac{T_2}{300} = \left(\frac{V_1}{\frac{V_1}{4}}\right)^{2.3302-1}$$

238 
$$\frac{T_2}{300} = \left(\frac{4V_1}{V_1}\right)^{1.3302}$$

239 Take the Ln of both sides and expand the equation accordingly. [You are advised to work it out](#)  
240 [for practice purpose.](#)

241 
$$T_2 = 1915.4 \text{ K}$$

242 *Attempt the following questions*

2. To what pressure must a given volume of nitrogen originally at 100 °C and 1 atm pressure be adiabatically compressed in order to raise its temperature to 400 °C.

3. One mole of Argon is expanded reversibly and adiabatically from 22.4 L at 25 °C to 44.8 L. Calculate the final temperature and pressure if the gas is assumed to be ideal.

### Isothermal process

This is a process where the temperature is maintained constant. i.e.  $\Delta T = 0$ .

Recall:  $C_v = \Delta E / \Delta T$ . Therefore,  $\Delta E = C_v \Delta T$

This means that the internal energy varies with temperature only. Therefore, when  $\Delta T = 0$  (isothermal),  $\Delta E = 0$ .

From first law:  $\Delta E = q - W$ . Since  $\Delta E = 0$ ,

$$q = W$$

To compress or expand a gas from  $V_1$  to  $V_2$  under pressure  $P$ ,

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

For an ideal gas,  $PV = nRT$ , Therefore,  $P = nRT/V$

$$q = W = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

Since  $T$  is constant,  $nRT$  is constant. Therefore,

$$W = nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$W_{max} = 2.303nRT \log \frac{V_2}{V_1} \dots \dots \dots (6)$$

This gives the maximum work obtainable in the isothermal reversible expansion of  $n$  moles of an ideal gas from  $V_1$  to  $V_2$  at constant  $T$ .

Equation (6) can also be changed to the pressure term by substituting  $P_1/P_2 = V_2/V_1$  according to Boyle's law. This gives:

$$W_{max} = 2.303nRT \log \frac{P_1}{P_2} \dots \dots \dots (6)$$

266 Example

267 1. Calculate the maximum work obtainable by the isothermal reversible expansion of 2 moles of  
268 nitrogen from 10 L to 20 L at 25 °C. Take  $R = 8.3142 \text{ J mol}^{-1} \text{ K}^{-1}$

269 Solution

270 Given:

271  $n=2$ ,  $V_1 = 10\text{L}$   $V_2 = 20 \text{ L}$   $T=25 \text{ }^\circ\text{C} = 273 + 25 = 298\text{K}$   $R = 8.3142 \text{ J mol}^{-1} \text{ K}^{-1}$ .

272 From the expression  $W_{max} = 2.303nRT \log \frac{V_2}{V_1}$

273 
$$W_{max} = 2.303 \times 2 \times 8.3142 \times 298 \log \frac{20}{10}$$

274 
$$W_{max} = 3435 \text{ J}$$

275 Try these questions

276 1. An ideal gas undergoes a reversible expansion from an initial volume  $V_1$  to a final volume  $10V_1$   
277 thereby doing 10,000 J of work. The initial pressure was 100 atm. (1) Calculate  $V_1$ . (2) if there  
278 were 2 moles of gas, what must have been its temperature.

279 2. Calculate the temperature of 2 moles of an ideal gas which undergoes a reversible expansion  
280 from an initial vol  $V_1$  to a final volume  $10V_1$  and thereby does 100 J of work.

281

## 282 Learning outcomes

283 In addition to the previously mentioned outcomes above, you should be able to:

- 284 • define heat capacity, derive and apply the equation connecting  $C_p$  and  $C_v$
- 285 • derive the equations for reversible adiabatic process and apply them in problem-solving  
286 calculations appropriately
- 287 • derive the expression for the work done in isothermal process and how to apply the  
288 expression for calculation purposes.

289