PRACTICAL WORK BOOK

MY-201 Metallurgical Thermodynamics and Kinetics



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Batch	
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Department of Metallurgical Engineering NED University of Engineering and Technology

PRACTICAL WORK BOOK

MY-201 Metallurgical Thermodynamics and Kinetics



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This is to certify that this practical book contains _____ pages.

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Department of Metallurgical Engineering NED University of Engineering and Technology

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Metallurgical Thermodynamic	s and Kinetics (MY-201) as prescrib	bed and appre	oved by Bo	ard of

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His/her performance is reflected by index/contents of his/her practical workbook. This overall performance of the student is Excellent/Very Good/Good (satisfactory)/Not Satisfactory

Course Teacher

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MY-201 Metallurgical Thermodynamics and Kinetics

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EXPERIMENT No. 1

OBJECTIVE:

Introduction to Thermodynamic Terms and Properties

BASIC DEFINITIONS:

1. Thermodynamics

This word is combination of two greek words thermo (heat) and dynamics (power/motion) that is thermodynamics is the study of heat related to matter in motion or is the study of the forces and motion caused by thermal conductivity.

2. Thermodynamic system

Thermodynamic system is defined as the quantity of matter or a region in space to which we focus our attention for the purpose of analysis.

a) Open system

A system in which both mass and energy either in the form of heat or work can enter or leave the system.

b) Closed system

A system in which only energy can enter or exit the system, mass cannot as it is fixed.

c) Isolated system

A system in which neither energy nor mass can enter or leave the system. It's a special case of closed system.

3. Surroundings

The mass or region outside the system is called surrounding.

4. Boundry

A real or imaginary surface that separates the system from its surroundings is called boundry of the system i.e boundry is the contact surface which is shared by both the system and the surroundings.

5. Thermodynamic Properties

Thermodynamic properties may be classified as intensive or extensive.

a) Intensive Properties:

Properties that are independent of size of the system i.e it's a property whose value is same for any part of the system as it does for the whole system.

b) Extensive properties:

Properties that depend upon the size or extent of the system.

QUESTIONS

1. A metal is placed in a furnace and melting is under process, which type of system is this, discuss and sketch diagram.

2. Boiling of water in and open pot is which type of system and why?

3. Enlist the extensive and intensive properties.

4. Comment on the validity of the following statements:

Body A and body B are at 50°C and the direction of heat flow is from body B to body A.

EXPERIMENT No. 2

OBJECTIVE:

Introduction to Thermodynamic Processes

PROCESS:

A change that a system undergoes from one equilibrium state to another is called a process. Process types

a) Isochoric process:

It is a process that proceeds in such a way that volume remains constant during execution

b) Isobaric process:

It is a process that proceeds in such a way that pressure remains constant execution

c) Isothermal process:

It is a process that proceeds in such a sense that temperature remains constant during execution.

d) Adiabatic process:

It is a process in which net energy in the system remains the same. No energy can flow in or out of the system.

QUESTIONS

1.Differentiate Isothermal and Adiabatic Process

Isothermal	Adiabatic

2. Sketch P-V and T-V Diagrams for all processes

EXPERIMENT No. 3

OBJECTIVE:

To calculate the Heat of Vaporisation (H_ν) of a liquid (e.g. Water) by using CLAUSIUS – CLAPEYRON Equation

THEORY:

The relationship between the vapor pressure of a liquid and the temperature is shown graphically as:



The same data, if "massaged", that is, expressed in a different manner, can be shown graphically as a straight line:



This linear relationship can be expressed mathematically as

$$\ln P = -\Delta H_{vap}/R(1/T) + C$$
 (1)

where ln P is the natural logarithm of the vapor pressure, ΔH_{vap} is the heat of vaporization, R is the universal gas constant (8.31 J·K⁻¹mol⁻¹), T the absolute temperature, and C a constant (not related to heat capacity). This is the *Clausius-Clapeyron equation*, which gives us a way of finding the heat of vaporization, the energy that must be supplied to vaporize a mole of molecules in the liquid state.

A plot of ln P vs. 1/T has the form of a straight line. Compare equation (1) to

$$y = mx + b$$

(2)

which is the equation for a straight line. In equation (1), lnP is y, 1/T is x, and $-\Delta H_{vap}/R$ is m. In this experiment, you will measure the vapor pressure of water over a range of temperatures, plot the data, measure the slope of the line, and then calculate ΔH_{vap} for water.

The method you will use to measure the vapor pressure will require careful readings of the volume of air and water vapor in an inverted graduated cylinder immersed in a beaker of water. You will half fill the graduated cylinder with water, and then immerse it upside down in enough water to cover the cylinder. Then you will warm the water in the beaker. As the temperature increases, the air in the graduated cylinder expands, and the vapor pressure of the water increases. Once the water in the beaker reaches a high enough temperature, the assembly is allowed to cool. A series of volume and temperature readings are taken, and then the water in the beaker is iced. At ice temperatures, the vapor pressure of water is negligible. The volume at that point is due to the air alone, within the limits of the measurements. This volume is recorded. Using the gas law equation, the number of moles of air in the cylinder is calculated:

$n = PV_{cold} / RT_{cold}$ (3)

Then, for each of the other temperatures and volumes measured, the pressure from this number of moles of air is calculated. The total pressure in the graduated cylinder is atmospheric pressure. The difference, then, between the pressure caused by the air and the atmospheric pressure must be due to the vapor pressure of water. This is an application of Dalton's law of partial pressure:

$$\mathbf{P}_{\text{total}} = \mathbf{P}\mathbf{1} + \mathbf{P}\mathbf{2} + \dots \tag{4}$$

EQUIPMENT:

Work in pairs
Special supplies:
1-1000 ml beaker with components
From your drawer:
1 thermometer
1 stirring rod
From the large drawer:
1 Bunsen burner

• Ring stand and hardware

PROCEDURE:

Assemble the components from the beaker on the thermometer as shown in the diagram. View the assembled apparatus at the instructor's desk as needed. Before placing the graduated cylinder/thermometer assembly into the beaker, fill the cylinder half full with deionized water. The beaker should have around 800 ml of deionized water in it. Now place the tip of your finger over the mouth of the cylinder, and invert the assembly and lower it into the beaker. Once the mouth of the cylinder is submerged into the water in the beaker, you can release your finger. Clamp the cork at the top of the thermometer so that the assembly is firmly in place. The inverted cylinder should be just above the bottom of the beaker, and the water in the beaker should just cover the top of the cylinder. Heat the beaker with a Bunsen burner turned on to its maximum heat output until the water reaches 72 to 75° C. Turn off the burner. The volume of entrapped gas in the cylinder should nearly fill the cylinder. If gas bubbles out of the cylinder at the top temperature, do not be concerned. Stir the water in the beaker, and record the temperature (to the nearest degree) and the volume of gas in the cylinder (to the nearest 0.01 ml).

Remember that the cylinder is inverted. In this diagram: the volume of gas is about 5.63 ml. The meniscus is exaggerated in the drawing.



Record temperatures and volumes every 5°C or so until you have 5 or 6 readings. You can hasten the cooling by adding small amounts of water or ice to the beaker, but the temperature in the beaker must be uniform when you make the measurements. This requires good stirring. After the 5th or 6th reading, it will be time to lower the temperature of the water in the beaker to below 5°C. Use a small beaker to remove about half of the water in the beaker, taking care that you do not disturb the water in the inverted cylinder. Fill the beaker with ice, and stir. If all of the ice melts, and the temperature is still above 5°C, remove more water, and add more ice. Stir the water in the beaker for a few minutes to allow the temperature of the water in the cylinder to equilibrate with the temperature in the beaker, and then make the cold temperature and volume reading

Take great care with this last measurement, because all of your data will become tainted if this reading is off.

CALCULATIONS:

Use the cold temperature data and equation (3) to find the number of moles of air in the cylinder.

Use $R = 62.4 \text{ L} \cdot \text{torr} \cdot \text{K-1mol-1}$. Convert the temperature to Kelvins, and the volume to liters.

Barometric Pressure:Torr			
Volume in ml	Temperature in C ⁰		

Table -1

Show the mathematical setup here:

n _{air} _____

Rewrite the volume and temperature data in the table-1,

converting the units to liters and Kelvins. For each of the higher temperature sets of volume and temperature, use the value for n just calculated, along with the V and the T, to calculate the pressure of the air using the gas law. Rearrange equation (3) so that P is isolated. After the pressure of air at each temperature is calculated, subtract the value from the atmospheric pressure recorded from the barometer. This will be the vapor pressure of water at that temperature. When you have calculated the vapor pressure and recorded it, press the *ln* button on your calculator, and record the ln P value in the table. Also calculate and record the value of 1/T for each temperature. You should round your calculated values to 3 significant digits.

Volume in Ltr	T in K	P _{air} in torr	P _{vapor} in torr	lnP	1/T in K

You will plot the last two columns of data from this table onto the graph on next page. After the points are placed on the grid, use a transparent ruler to draw the best straight line through the points. Draw the line so that it extends the full width and height of the grid. It is possible, even likely, that none of the points will actually touch the line you draw. If you look at the line by holding the paper up so that you are sighting along the line from one of its ends, then the points should appear evenly scattered about the line. After the line is properly placed, make two marks on the line, one near the extreme left, one near the extreme right side of the line. If possible, make the marks where the line crosses the intersection of two grid lines. Make marks different from the marks used to show the actual data points.

The coordinates of the left mark will be x_1 and y_1 , the coordinates of the right mark will be x_2 and y_2 . Write $x_1 y_1$ by the left mark and $x_2 y_2$ by the right mark.

From the line: $Y_2 =$ ____, $Y_1 =$ ____, $X_2 =$ ____, $X_1 =$ _____

Calculate the slope: $Y_2 - Y_1 / X_2 - X_1 =$

Be careful to use the exponents on the x terms. The graph begins with the number 2.80. Notice that the label on the x-axis applies the exponent 10^{-3} to the numbers. The slope will be a large, negative, number. Enter your data points into the Clausius-Clapeyron Excel template on one of the computers, and obtain a computer-generated graph and slope calculation printout. Use this to see how well you placed the line by hand. Include this printout with your Workbook. Make sure you put the names of the partners and the date on the graph.

From equation (1), (Use $R = 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

% Error = ΔH_{exp} - $\Delta H_{book}/\Delta H_{book} \ge 100$

% Error = _____

The book value for ΔH_{vap} at the temperatures of the experiment is ______ J-mol⁻¹. Calculate the % error in your measured value:

The slope = $-\Delta H_{vap}/R$

The % error tends to be high. One major problem is that the vapor pressure does not reach its equilibrium value. This makes the value of the heat of vaporization higher than it should be. A solution to this problem is to do the measurements in an evacuated container. Equilibrium vapor pressures are attained more rapidly in the absence of air.

QUESTIONS

1. The two point version of the Clausius-Clapeyron equation is $lnP2/P1=-\Delta Hvap/R(1/T2-1/T1)$. Use this equation and the following data to calculate ΔH_{vap} of water: At 20°C, the VP of water is 17.5 Torr. At 60°C, the VP of water is 149.4 Torr (Use R = 8.314 J·K⁻¹·mol⁻¹).



EXPERIMENT No. 4

OBJECTIVE:

To compare the diffusivity of Gase, Liquid, and Solid by experimentally determined values of their respective Diffusion Coefficients (D).

The objectives of these experiments are to show that the subject of diffusion is not really so hard to understand and that it plays an important role in our daily lives. Diffusion of molecules through the air can be determined using our sense of smell. Liquid diffusion can be observed using a paper towel or ink in water. Solid diffusion can be observed by measuring the movement of the coloration of a dopant ion in a glass stirring rod or dyes in plastic glue sticks. The objectives, then , are to measure the diffusion rates for solids, liquids, and gases using simple techniques to yield sophisticated answers. Diffusion coefficients will be determined, and curve fitting the graphical results will be performed.

EQUIPMENT :

- (1) Metallurgical preparation and polishing apparatus,
- (2) Glass or quartz stirring rods,
- (3) Cupric chloride, Petri dishes, test tubes, tongs, bunsen burners, small beakers,
- (4) Food Coloring, vanilla or garlic extract, paper towels (grocery store),
- (5) Metallurgical microscope,
- (6) Timers (split time preferred), and
- (7) Hot melt clear and colored glue sticks.

THEORY:

Solid state diffusion plays many roles in the modern world. It make it possible to control impurites in semiconductors, sinter metallic and nonmetallic particles, oxidize various materials, control surface alloying of metals, color minerals and gemstones, and make solid state lasers work, to name a few. The process is dependant on high temperature of the solids, the higher the temperature, the more vibration occurs that allows the atoms to let the diffusant through. For instance, arsenic in silicon will not diffuse at room temperature and will diffuse only a few micrometers after 3 hours at 1000oC. Clearly, solid state diffusion plays a major role in many facets of our lives. The odor of a skunk reaching our nose (sensor for smell), even when there is no wind coming from that direction immediately brings to mind the diffusion of gases. The time to detect the odor at room temperature over a 10 meter distance might be as long as ten seconds. If diffusion of gaseous molecular species is said to proceed at velocities of up to 103 m/s, why do we not smell things almost instantaneously? As in the case of solids, the atoms or molecules of the "host" gas "get in the way" (the atoms are separated by approximately 100 nm, making the time of diffusion appreciably longer than if there were no gas present.

The diffusion of liquids in liquids is slower than in gases, due to the lower kinetic energy of the liquid itself. The atoms or molecules are closer together, providing for a path with many more collisions per unit length than the case of gaseous diffusion. For instance, the time necessary to diffuse a drop of food dye in water from the center to the edges of a 20 cm. container might be a few minutes at room temperature.

The diffusion of a species in a solid is the slowest of all. The spaces between molecules or atoms is small (of ther order of a few tenths of a nanometer) and, therefore, the temperature necessary to allow diffusion of impurities over some small distance in a reasonable time is high. The cases which involve the diffusion of liquids or gases in solids, or gases in liquids are governed by similar laws of kinetics and have distinct proportionality constants, called diffusion coefficients, for each separate case. In all cases, diffusion has a driving force or forces which govern how fast the diffusiont will travel in the

host substance. Some of the factors governing the delivery of the energy necessary to make this happen are: gradients in pressure, gradients in temperature, pressure, temperature, size of the molecule, kinetic energy of the molecules (both diffusant and host), spacing of the molecules of the host, defects in the host, electric fields (voltage gradients), and photonic effects.

A theoretical background describing diffusion and the equations which govern it may be found in the Appendix at the end of this paper. The diffusion coefficient, D, will be proportional to the distance by the following formula

 $X_{1/2} = sqrt (Dt) \qquad Eqn (1)$

where $x_{1/2}$ is the distance at which the concentration is 1/2 of the initial concentration of the diffusant racked, and t is the time at temperature or the time of diffusion.

EXPERIMENT:

1. DIFFUSION OF TWO GASES

In order to perform this experiment, five students will need to stand in line with an "interperson spacing" of one meter (shown in Figure 1) in a relatively draft-free room (Note: A draft is a form of force changing the diffusion velocity). Person #1 will drop a few drops of vanilla or garlic extract onto a paper towel or cotton cloth, at which time all will start their stopwatches. As each person detects the odor of the vanilla or garlic, he/she should stop the stopwatch and record the time in Table 1 below. The paper towel should then be sealed in a plastic bag, brought out of the room, and disposed of properly. A second and third trial should be performed and recorded, disposing of the towel as before. Average the sets of data and plot distance vs time. Calculate (estimate) a diffusion coefficient for this experiment. Curve fit the plot for a polynomial and an exponential. Calculate the velocity of the diffusant gas in the room air.



2. DIFFUSION OF TWO LIQUIDS

Set a Petri dish or shallow Corning Ware dish on top of a bullseye (shown in Figure 2) in the center of an overhead projector platen.

Pour to approximately 10 mm depth cold water in the dish and allow it to settle and stop all motion. Put a 20% (vol.) aqueous solution of food coloring or ink in propylene or ethylene glycol (antifoaming and wetting agent) with this solution. Lower the dropper about 2mm below the surface of the water and squeeze a drop carefully into the water in the center of the bullseye. Start timing the color front movement as it passes each ring of the bullseye and record the time corresponding to the distance reached in a table like the one shown in Table 2. Using the overhead projector will enhance the student's ability to estimate the movement.



Figure 2 Water-filled dish on projector with bullseye

Average the three trials and estimate the diffusion coefficient for this experiment. You may do the same with "hot" water and see if the results are different. Calculate the velocity of the dye in the water.

3. DIFFUSION OF A LIQUID INTO A SOLID

CAUTION: This experiment will produce HCl gas and should be performed under a fume hood for safety. Gently heat a Pyrex test tube, vertically clamped to a ring stand, which is approximately 1/3 filled with CuCl₂ . 2H₂O, over a bunsen burner until the cupric chloride just melts (435°C). This experiment can also be performed using a small beaker heated on a hot plate. Score and cut a quartz or glass rod to a length approximately 4 cm longer than the test tube or beaker. Carefully place the glass rod into the test tube or beaker and leave it at this temperature for 10 to 15 minutes. Remove the rod and allow it to cool on a flameproof laboratory fiber board. Score and cut the end of the rod to expose a "clean" cross section of the

diffused couple. Wash the rod in running water until it is clean. Measure the "depth of diffusion" of the Cu⁺⁺ ion into the glass. Estimate the diffusion coefficient for this experiment.

Do this experiment for multiple times at this temperature (example in Table 3) and record the data. Calculate the velocity of the diffusant into the glass rod material.

If you have a non-corrodable thermocouple, you may perform the experiment at various temperatures slightly below the melting point of the cupric chloride and estimate an activation energy of diffusion.

(Optional)

It is also interesting to put two glue gun sticks (polypropylene), one colored and one clear, in a test tube or aluminum foil boat which just fits them (approximately 1 cm.) and mark their interface on the tube or foil. Place the test tube on a small ring stand and put it into an oven for 10 minutes or so at a temperature above its melting point (approximately 140°C). Take the samples out and let them cool to room temperature. Have the students make their own observations. What is the same and what is different when the above experiments are compared with this one involving the glue sticks?

Distance in m	Trial 1 sec	Trial 2 sec	Trial 3 sec

Table-1 : Difffusion of Gasses Data

Table 2 :Diffusion data for liquids

Distance in mm	Trial 1 sec	Trial 2 sec	Trial 3 sec
5			
10			
15			
20			

Table 3 : Data for solid diffusion

S. No.	Depth of Diffusion in mm	Time of Diffusion in min	Tempertaure of Diffusion in min
1			
2			
3			

REPORTING:

The student should not only write his or her findings, but should suggest variations of these experiments for other substances and methodologies. Order of magnitude values for the diffusion coefficient (in m_2/s) for the three experiments are as follows:

(a) gaseous, ~ 10^{-1} , (b) liquid, ~ 10^{-6} , (c) solid, ~ 10^{-11}

Reports should be judged on the basis of not only data "correctness" but on the basis of suggestions for improvement, error sources and estimates, observations, etc.

AN OVERVIEW OF DIFFUSION MECHANISMS AND THEORY:

A knowledge of mass transfer mechanisms is essential for the description of how atoms (molecules) move in solids, liquids and gases. The diffusing species make use of vacancies in order to move around in the host substance. In fact, when there are line vacancies, the atoms move at a much faster rate down the "pipe", as can be seen in the case of grain boundaries in solids. For point vacancies, an equilibrium number of vacancies, and hence the number of "atom jumps", can be calculated by determining the amount of energy, or **activation energy**, 'E, necessary for an atom to leave a lattice site and create a vacancy. It can be shown by Boltzman statistics that, given a total or initial number of atoms, ni, a fraction of these, n, at a given temperature, attain sufficient energy to escape from regular lattice points and create vacancies. The energy is related to this fraction by

 $n/n_i = C \exp(-\Delta E/kT)$ Eqn(A1)

or in semi-logarithmic plotting of n vs 1/T, a straight line with slope -'E/k, where C is a constant dependent on the material, k is Boltzman's constant (1.38 x 10-23 J/K), T is the absolute temperature in degrees Kelvin, 'E is the activation energy in Joules. Stated simply, if a bar of material composed of two materials in solution along which there is a gradient in composition is heated to a temperature above room temperature (usually near its melting point), the solute atoms will become redistributed,

attempting to make the composition more uniform. Thermal energy supplies the the atom or molecule with sufficient vibrational energy to allow the solute atoms to move from a region of higher concentration to one of lower concentration.

In one dimension, considering a segment of solid 'x, shown in Figure A1(a), the concentration of solute at x_0 is C_0 and the concentration of solute at x_1 is C1. The non-steady state condition is shown in Figure A1(b) for increasing times. The diffusion flux J12 is the amount of material passing through a unit area in the x- direction per unit time and is proportional to the concentration gradient dC/dx by

Fick's first law as

$$J_{12} = -D dC/dx \qquad \qquad Eqn (A2)$$

where D is the proportionality constant called the **diffusivity** or **diffusion coefficient**. This is more generally stated as Fick's second law

$$dC/dt = d/dx(D dC/dx)$$
 Eqn (A3)

for the general case where D is concentration dependent under non-steady state conditions. Solving these equations for the boundary conditions

(a) At t = 0, C = 0 for all x>0,
(b) At t = 0, C = C₀ for all x<0, and
(c) At x = 0, C not = C₀ for all t>0, gives

$$C = C_0/2[1 - erfc(X/2(sqrt Dt))]$$
 Eqn (A4)

where **erfc** refers to the **Gaussian error function**. The point at which the concentration of the diffusant is 1/2 of the initial concentration gives a simple relation most often used by scientists. This relationship is given in the body of this paper and may be used for the desired calculation of the diffusion coefficient. The diffusion coefficient, on the other hand, varies with temperature according to an Arrhenius-type of equation,

$$D = D_0 \exp(-E_A/kT) = a_2 (E_A/Nh)\exp(-E_A/kT)$$
 Eqn (A5)

where a is the interatomic distance, N is Avogadro's number, h is Planck's constant (6.6 x 10^{26} atoms per kilogram mole). The values of D₀ for a number of solid materials are given in any number of reference books and papers on the subject.







Figure A1 Diffusion of Atoms

EXPERIMENT No. 5

OBJECTIVE:

The present experiment is aimed at finding an average value of heat transfer coefficient under different fluid flow conditions.

THEORY:

Heat exchange between the solid and fluid is said to occur due to convection whenever there is a difference in temperature between two phases and there is motion in the fluid. If the motion of the fluid is caused by the buoyancy forces which arise due to variation in the density of the fluid with temperature, the process is called free or natural convection. If the motion of the fluid is caused by external means such as blower, wind, fan or pump, the process is called as forced convection. Heat exchange due to convection may be described in terms of a heat transfer coefficient 'h' by Newton's law of cooling as:

$$Q=Ah(T_s-T_f)$$

A is the area of the solid-fluid interface, T_S and T_F are the solid and fluid temperatures respectively. The value of heat transfer coefficient could depend upon the following factors:

(a) Type of the fluid motion.

(b) Properties of the fluid used.

(c) Geometry of the solid-fluid interface.

(d) Difference in temperature between the solid and that of the fluid.

(e) Position along the surface of the solid body.

On the assumption that there is no variation in temperature within the solid body, heat balance gives

$$M C_p dT_s/dT = -Ah (T_s-T_f)$$

M is the mass of the solid body and C_P is the specific heat capacity of the solid. Solving the differential equation by taking the initial temperature of the solid as T_1 , one may obtain temperature, T_t as a function of time as follows:

$$\theta_{t} = (T_{t} - T_{f})/(T_{1} - T_{f}) = \exp(-hAt/MC_{p})$$

The above equation shows that the plot of ' $\ln\theta_t$ ' versus time 't' will be a straight line with a slope (hA/MC_P). Heat exchange area 'A' may be obtained from the dimensions of the solid. M is the mass of the solid. Heat capacity data, C_P is made available from the literature. This lumped parameter solution is reported to be valid as long as the dimensionless Biot number is less than 0.1, i.e.

$$B_I = hL/K < 0.1$$

K is the thermal conductivity of the solid and L is the characteristic length of the body, i.e. the volume to interface area ratio. If the Biot number is greater than 0.1, variation in temperature within the solid body may no longer be ignored, and solution of the following differential equation must be considered:

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right] \text{ or } \frac{\partial T}{\partial t} = \alpha \nabla^2 T$$

A three dimensional numerical solution, even in simple cases, requires help of computer. In practice we reduce a three dimensional problems to one dimensional one. This is achieved by making the body an infinite (very large length) cylinder or an infinite slab (with finite thickness and very large surface) etc.

The above equation in one dimension becomes

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$

HEISLER CHART:

The solution of the equation is given in the chart (attached). The following dimensionless numbers and graphs are frequently used:

 Θ (Dimensionless Temperature) = (T_t - T_f)/ (T₁-T_f) Biot Number = hL/K (W/m² °C)

- L = Characteristic dimensions of the body (m)
 - $=\frac{1}{2}$ thickness of a plate.
 - = Radius of a cylinder.
 - = Radius of a sphere.
- K = thermal conductivity (W/m $^{\circ}$ C)

Fourier number $Fo = \alpha t/L^2$

- α = thermal diffusivity = K/ ρ C_P (m²/s)
- ρ = density (Kg/m3)

The solution of the equation takes the form

 $\Theta = \Psi$ (Bi, Fo, x/L)

x = coordinate of the point in the body at which temperature or time is to be determined. First determine Fo and Biot number from the physical properties of the body. Read the temperature Θ for these Biot and Fourier numbers.

PROCEDURE :

- 1. Note down the room temperature and the temperature of the water bath.
- 2. Measure diameter, length and mass of the aluminum cylinder.
- 3. Attach the junction of the thermo-couple to the aluminum cylinder.
- 4. Lower the cylinder to the uniform temperature zone of the furnace.
- 5. Connect the open ends of the thermocouple wires to mili-voltmeter or the X-Y recorder.
- 6. Select the appropriate range of the measuring instrument as well as the time scale of the recorder.
- 7. Wait till the temperature of the cylinder has reached a steady value.

8. Take out the cylinder with the hot junction of the thermocouple still attached to it from the furnace and allow it to cool in the selected medium.

9. Note or record the temperature as a function of time till it has cooled to around 200°C or less.

10. Repeat steps 3 to 9 for each of the three medium, i.e. still air, forced air and water bath.

REPORT:

1. Plot temperature versus time for all experiments on one graph paper.

2. Plot the dimensionless temperature, i.e. $(Tt - T_F)/(T_I - T_F)$ versus time and $\ln[(Tt - T_F)/(T_I - T_F)]$ versus time in all cases.

3. Determine the slope of the line, i.e. $(hA/M C_P)$ from the plot in step 2 above.

4. Calculate the heat transfer coefficient 'h' and Biot No. i.e. (hL/K) from the slope.

5. Determine the heat transfer coefficient using Heisler's chart.

DATA

	Units	Aluminum	Air	Water
Density	Kg/m'	2700	1.18	1000
Specific Heat Capacity	J/Kg⁰K	896	1.006	4180
Thermal Conductivity	J/ms K	204	0.026	0.597

DTA SHEET :

Date of Experiment:	Room Temperature:°C
Water Bath Temperature:°C	Length of the cylinder: mm
Diameter of the cylinder mm	Mass of the cylinder g

Air		Forced Air		Water	
Time	Temperatur	Time (min)	Temperature	Time	Temperature
(min)	e (°C)		(°C)	(sec)	(°C)
0		0		0	
0.5		0.5		2	
1		1		4	
2		1.5		6	
3		2		8	
4		3		10	
6		4		15	
8		6		20	
10		8		25	
15		10		30	
20		12		40	
25		14		50	
30		16		60	



EXPERIMENT -6

OBJECTIVE:

The experiment is aimed at finding the standard free energy, enthalpy and entropy of formation of calcium carbonate through pressure measurement technique.

THEORY:

Decomposition of calcium carbonate may be represented as follows:

$$2CaCO3(s) = 2CaO(s) + 2CO2 \qquad K = P_{CO2}$$

Activity of solid species may be taken as unity as these are present in pure form. The standard free energy for the reaction is related to the equilibrium constant as follows:

$$\Delta G^0 = - RT \ln K = - RT \ln P_{CO2}$$

Standard enthalpy and entropy changes for the reaction are related to the standard free energy change as described below:

$\Delta \mathbf{H}^{0} = \partial \left(\Delta \mathbf{G}^{0} / \mathbf{T} \right) / \partial (1 / \mathbf{T})$	$\Delta \mathbf{H}^{0} = - \mathbf{R} \partial (\ln \mathbf{P}_{\rm CO2}) / \partial (1/T)$
$\Delta S^0 = \partial (\Delta G^0) / \partial (T)$	$\Delta S^{0} = - R \partial (T \ln P_{CO2}) / \partial (T)$

PROCEDURE:

The apparatus for the study on decomposition of Calcium Carbonate is shown below:



Follow the steps given below:

- 1. Place about 20g of Calcium Carbonate in the silica tubing one end closed.
- 2. Keep the reaction tube in the furnace and bring it to around 300°C.
- 3. Evacuate the system using the vacuum pump to around 0.1 mm Hg level.
- 4. Close the stopcock connection to vacuum pump.
- 5. Set the temperature controller of the furnace at 760°C

6. Record the changes in the temperature of the furnace and levels of mercury in the two legs of manometer

- at regular intervals of 2 minutes.
- 7. Repeat the experiment at 800° C and 840° C

The partial pressure of carbon dioxide in the reaction tube at any instant is related to the difference in the mercury levels in two legs of the manometer as follows:

= [barometer pressure in mm Hg – manometer reading in mm Hg] / 760Barometer pressure may be obtained from the barometer fixed in the walls of the laboratory.

REPORTING:

1. Plot ln *CO*2 *p* versus (1/T) to find value of Δ H° for the reaction.

2. Plot (T ln CO2 p) versus T to get value of ΔS° for the reaction.

3. Determine from your data the temperatures at which calcium carbonate would decompose when heated at one atm.

DATA SHEET:

Time, min	Temperature, °C	Temperature, K	Manometer Left Leg, mm Hg	Manometer Right Leg, mm Hg	Pressure Difference, mm Hg

EXPERIMENT-7

OBJECTIVE:

The experiment is aimed at knowing the rates of oxidation of Cu in atmospheric air by the weight gain method.

THEORY:

The oxygen must diffuse across the oxide layer to keep the process of oxidation going or the metal atoms must diffuse out of the film and react with the atmospheric oxygen. The flux of metal or oxygen atoms for the reaction can be determined from the Fick's laws of diffusion. For a planer surface, net increase in weight due to the oxidation reaction is given as follows.

$$Kt = [\Delta m/A]^2$$

Where Δm is increase in weight of sample (g). A is surface area (cm₂). t is time (sec). and k is constant (g₂/cm₄sec₁).

PROCEDURE:

1. Take three strips of copper and clean each with an emery paper and then in an acid (dil. HNO₃) solution followed by running water. Dry each strip carefully.

2. Attach the empty bucket with the hanging wire to the balance and insert the bucket into the furnace at 550_oC. Take reading after 3 min.

3. Take out the empty bucket and place one of the strips on it and insert it into the furnace. Take reading after 10, 20 and 30 minutes of time interval.

4. Repeat steps (2) to (4) at two other temperatures i.e. 650_oC and 750^oC.

REPORT:

Report tabulated experimental results. From the results plot/calculate the following -

(a) Plot $[\Delta m/A]$ and $[\Delta m/A]^2$ versus time and find the value of k in the equation above and compare it for Cu and mild steel.

(b) Plot log $[\Delta m/A]$ and 1/T of for given periods of oxidation (T is temperature in K) and discuss significance of this plot.

- (c) Plot log $[\Delta m/A]$ versus log[t] for all temperatures.
- (d) Derive the equation (1) starting with the laws of diffusion and mention the assumptions made.

(e) Calculate the thickness of the oxide film which forms at all temperatures from the above data. Use density of Cu₂O as 6 g/cm^3

DATA SHEET :

Weight of the empty bucket (g)	Weight of the bucket + Strip (g)	Difference of the weight (g)	Time (sec)	Initial weight of the metallic strip (g)	Weight gain of the metallic strip (g)	[Δ <i>m/A</i>] (g/cm ²)	$\frac{[\Delta m/A]^2}{(g^2/cm^4)}$	Log(time)
	·			550 ⁰ C				
			0					
			600					
			1200					
			1800					
				650 ⁰ C				
			0					
			600					
			1200					
			1800					
	·			750 ⁰ C				
			0					
			600					
			1200					
			1800					

EXPERIMENT-8

OBJECTIVE:

The aim of the experiments is to study the kinetics of roasting of ZnS by weight loss method.

THEORY:

The sulphide ores are in general difficult to reduce to metal. Therefore, it is desirable to convert the sulphide form of the ore to oxide form, which is suitable for reduction. This conversion is carried out by heating the sulphide ore below its fusion temperature with excess of air.

2ZnS + 3O2 = 2ZnO + 2SO2

This is a typical roasting operation. The most general definition of roasting is as follows: Roasting is a metallurgical process in the extraction circuit wherein the ore is heated below the fusion point of its constituents under such conditions such that the metal component of the ore which is sought to recover will be chemically as well as physically changed from that form in which it occurs in the ore to some other form which will be amenable to same definite subsequent treatment for extraction of the metal. There are various types of roasting operations possible. The four important ones are (i) oxidizing roasting, (ii) reduction roasting, (iii) sulphate roasting and (iv) chloridizing roasting. As the name suggests oxidizing roasting is carried out to burn out sulphur from sulphides and replace them in whole or in part with oxides. The reaction may be expressed as:

$$MS(s) + 3/2 O_2(g) = MO(s) + SO(g)$$

Where M is a bivalent metal.

In industrial practice, roasting operations are carried out in various types of furnaces such as shaft furnace hearth roaster, rotary kilns and fluidized bed reactors. All roasting operations involve heterogeneous chemical reaction, that is to say, gas-solid reactions in which a solid reacts with a gas to produce another solid and gas, and therefore, the kinetics of a roasting operation should conform to the kinetics of gas solid reactions.

MATERIALS AND EXPERIMENTAL PROCEDURE:

Materials required for this experiment includes (a) Zinc sulphide, (b) oxygen and (c) nitrogen/ argon.

1. Weigh about 0.60 gm of the dry ZnS pieces, in the wire mesh basket.

2. Flush nitrogen/argon in the furnace tube already heated to give steady state temperature for 5 minutes to drive out air from it.

3. With the help of a thin nichrome wire slowly lower the basket containing zinc sulphide into the furnace. The other end of the wire is attached to the pan of a balance which is used to measure weight loss of the concentrate during the roasting operation with removing it from the furnace. The wire should be freely suspended into the furnace.

4. Note down the weight reading on the balance.

5. Switch off nitrogen/argon and start flushing oxygen at a given slow rate taking care to avoid any carry over of the ZnS particles.

6. Immediately start taking the weight readings at intervals of 2 minutes till almost a constant weight reading is obtained.

7. Note the temperature and oxygen flow rates before and after the experiments. Try to maintain them constant as far as possible throughout the experiment. In case of variation, average values of temperature and oxygen flow rates may be used.

8. Repeat the above for two other temperatures with the same flow rate of oxygen. (Suggested temperature 600° C, 650° C and 700° C)

REPORTING:

Upon roasting of ZnS, any of the following 3 products are likely to form according to phase equilibria in Zn-S-O system.

Reaction	Log K (K is equilibrium constant)			
	T = 900K	T = 1000K	T = 1100K	
$ZnS+3/2 O_2 = SO2 + ZnO$	21.77	19.19	17.07	
$ZnS + 2O_2 = ZnSO_4$	26.61	22.16	18.61	
$3ZnS+11/2 O_2 = ZnO_2ZnSO_4 + SO_2$	75.84	64.35	54.97	
T. R. Ingraham and H.H. Kellogg: Trans. of Met. Soc. AIME, Vol.227(1963), p.1419				

In addition, this roasting reaction is exothermic leading to significant, rise of sample temperature during oxidation.

Also insitu sintering of sample during oxidation is likely. All these make the kinetics complex. The following procedure for reporting is suggested.

1. Assuming the product to be ZnO, calculate fractional conversion (F) as function of time from your weight loss data.

2. From oxygen flow rate and weight loss data, calculate average value of SO_2 P in exit gas at one of the temperature. Then do thermodynamic calculations to predict about product.

DATA SHEET:

Weight of dry ZnS pieces =	g	Weight of ZnS pieces af	ter N2 purging = _	g
Initial N2 flow rate =	c.c/min	Initial O2 flow rate	=	c.c/min

Initial furnace temperature (°C)	Time (min)	Weight of zinc sulphide (g)	Corresponding furnace temperature(oC)	Corresponding oxygen flow rate (c.c./min)
600				
000				
650				
050				
700				
700				

EXPERIMENT-9

OBJECTIVE:

(a) To determine the decomposition voltage of aqueous solutions of ZnSO4.

(b) To determine current efficiency by using aqueous solution of CuSO₄.

CIRCUIT:

The basic circuit to be used as follows. Fig:1





THEORY:

The relationship between applied potential and the current flowing in an electrolytic cell usually take the characteristic shape shown in figure 2. The decomposition voltage for the electrolyte is obtained by extending the linear portion of the curve to the voltage axis. The points V₁ and V₁₁ on the figure 2 are the decomposition voltage for aqueous solution and fused salt respectively. As shown in the figure the residual currents (that is current obtained below the decomposition voltage) for fused salts can be significant. For aqueous solution, however, these are generally at very low so that the onset of decomposition is indicated rather sharply.

Beyond the decomposition voltage, the variation of current with voltage will be linear. However, current cannot be increased infinitely because, for given electrolyte and a given electrode surface area, there is a limiting current. Thus, beyond a maximum value of voltage, the current should become constant.

$$\Delta G = - ZFE$$
 Eqn(1)

Where,

 ΔG = - Changes in free energy due to the electrolysis reaction, Joules / mole

Z = Valency,

F = Faraday constant (96500 columbs / volt gm equivalent)

E = Reversible E.M.F. of the cell, volts

Again

$$\Delta G = \Delta G^0 + RT \ln J \qquad \text{Eqn}(2)$$

Where, J = activity quotient Hence

$$E = E_0 - (RT / ZF) \ln J$$
 Eqn(3)

Where E_0 is reversible e.m.f. of the cell under standard conditions (activities of all species are 1 & Temperature = 298 K).

R = 8.314 J / mole K

$$E^{0}_{cell} = E^{0}_{anode} + E^{0}_{cathode} \qquad Eqn(4)$$

Where E^{0}_{anode} and $E^{0}_{cathode}$ are standard single electrode potentials of anode and cathode respectively (available in standard electro-chemistry texts).

CuSO4: In electrolysis of an acidified aqueous solution of copper sulphate using copper as cathode and lead as anode, copper is deposited on the cathode and oxygen evolves at anode. The reactions are:

Adding:

$$Cu^{2+} + H_2O = Cu + 1/2 O_2 + 2H^+$$
 $E^0C_{ell} = -0.892 V$

$$E_{cell} = E_{cell}^{0} - [RT \ a_{Cu} x \ (P_{o2}) x \ (a_{H+})^{2}/2F \ (a_{Cu2+})] \quad Eqn(5)$$

Since $a_{Cu} = 1 P_{o2} = 1 atm$.

We have

$$E_{cell} = -0.892 - [RT \ln (a_{H+})^2/2F (a_{Cu2+})]$$
 Eqn(6)

 a_{Cu2+} and a_{H+} can be taken equal to concentration in mole per litre which can be calculated from concentration of Cu SO₄ and H₂SO₄ in the electrolyte.

ZnSO4: Coming to electrolysis of ZnSO4 and H₂SO4 solution with Zn cathode and Pb anode. The reactions are:

Zn Cathode:	$Zn^{2+} + 2e = Zn$	$E^0 = -0.763 V$
Pb anode:	$H_2O = 1/2 O_2 + 2H^+ + 2e$	$E^0 = -1.229 V$
Adding	$Zn^{2+} + H_2O = Zn + 1/2 O_2 + 2H^+$	$E^0_{\ cell} = -1.992 \ V$

$$E_{cell} = -1.992 - [RT \ln (a_{H+})^2/2F (a_{Zn2+})]$$
 Eqn(7)

Experimentally measured decomposition voltage should match with Ecell as calculated, from Eqs.(6) and (7).

PROCEDURE:

A: CURRENT EFFICIENCY

- 1. Carefully weigh a clean copper cathode.
- 2. In the cleaned vessel, take a mixture of M/5 CuSO4 and M/5 H₂SO4 solution.
- 3. Introduce the Pd anode and Cu cathode into the solution.
- 4. Pass 40 mA current for $\frac{1}{2}$ an hour.
- 5. Take out the cathode, clean and dry with distilled water and acetone and weight it.

B: DECOMPOSITION VOLTAGE

1. Set up the circuit as shown in the sketch.

- 2. Clean anodes and cathodes.
- 3. In a clean vessel, take one liter of an M/5 ZnSO4 solution: Add 1 ml of M/5 H2SO4 to it and stir.

4. Introduce Pb and Zn plates: Pass current for 5 minutes: wait for 10 minutes. On open circuit to bring the electrodes in equilibrium. At 4 ml more of M/5 H₂SO₄ and stir. Wait 5 minutes.

- 5. Read this open circuit voltages.
- 6. Set the voltage of the D.C. power supply lower than the above voltage and close the circuit (make sure that there is high resistance in circuit).
- 7. Note the direction of current. Set the voltage such so as to reach zero current.
- 8. Wait 5 minutes and take this cell voltage reading. Shake the electrodes once or twice.
- 9. Increase the voltage of D.C. power supply as well as variable resistance setting in steps to obtain different values of current. At each setting wait for few minutes and also shake electrodes once for stirring.
- 10. Note current and cell voltage at each setting upto 5 mA Max. (6 points).
- 11. Decrease current in steps and take a few readings.

REPORTING:

(a) Plot current vs Cell voltage curve for ZnSO4 solution and find out the decomposition potential.

(b) Calculate the E_{cell} from eqn. (7) and compare its absolute value with the experimentally measured decomposition voltage.

- (c) Compare the above values with the open circuit voltage also.
- (i) Calculate current efficiency.
- (ii) Discuss your results.
- (iii) Discuss why hydrogen does not evolve during electrolysis of Cu.