1.05 CARBON MONOXIDE / CARBON DIOXIDE EQUILIBRIUM

(4 points)

Outline

Reactions between a solid and a gas can conveniently be studied by a flow method, in which a stream of gas passes through a bed of solid at a fixed temperature. The flow rate is kept low enough that equilibrium will be attained, and analysis of the effluent gas gives the data necessary for calculation of the equilibrium constant.

In this experiment you will use this method to find the equilibrium constant for the reaction between carbon monoxide, carbon dioxide and carbon as a function of temperature. The enthalpy of reaction is calculated using the van't Hoff isochore. Experimental results are compared with values calculated by the so-called "Third law method", using literature values of thermodynamic parameters. The rate of reaction is rather low, and falls rapidly with decreasing temperature, so, as the gas emerging from the furnace cools quickly, no steps are taken to "freeze" the equilibrium mixture.

Background Information

This experiment relies upon ideas which you have met in the 1st year course on Classical Thermodynamics. The web page for the experiment is at: http://ptcl.chem.ox.ac.uk/~hmc/tlab/experiments/105.html

Safety / COSHH

Carbon monoxide is odourless and poisonous. Do not breath in the exit gases from the oven, being careful if you need to disconnect the bubble meters. Safety data for the chemicals in this experiment can be obtained through the web site given above and summary information is given at the end of these instructions.

Preparation

Before starting the experiment, read these instructions fully, and visit the Laboratory to see what the apparatus looks like. The purpose of the experiment is to gather data which can be used to calculate an equilibrium constant, so remind yourself how you can calculate the equilibrium constant for a gas phase reaction and how the variation of the value of the equilibrium constant with temperature can be related to the enthalpy change during the reaction.

Apparatus

A silica tube containing a bed of charcoal granules is heated in a furnace provided with an electronic temperature controller. The temperature of the bed is determined using a high temperature thermocouple.

Carbon dioxide is fed through the charcoal bed, and the gas emerging after reaction is analyzed by a pair of soap bubble flow meters. Although simple, this type of meter is still one of the most effective means of making accurate measurements of gas flow. Gas enters the bottom of a graduated glass tube, much like a segment of a burette, and flows up it. By squeezing a rubber teat containing soap solution at the bottom of the tube, a soap film is formed across the tube, whose rate of movement up the tube gives directly the rate of gas flow.

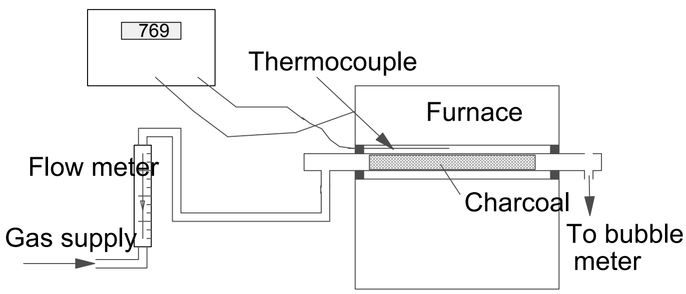

Fig. 1. The flow tube, controller and oven.

After leaving the flow meter, the $CO + CO_2$ mixture passes through a soda-lime scrubber, which removes CO_2; the CO left is then measured using a second flow meter.

The furnace temperature controller is a three term PID device (Proportional / Integral / Differential) operated with a chromel/alumel thermocouple placed by the charcoal bed. The thermocouple generates a large EMF, which is an almost linear function of temperature. This EMF is compared to the EMF of the thermocouple at the required temperature to give a difference known as the error signal. This signal is used to determine the energy that must be input to the furnace through a combination of three terms.

The *proportional input* provides a heating current directly proportional to the error signal. The *integral input* generates a current dependent upon the integral of the error signal with time - the longer a difference between the desired and actual temperatures has persisted, the greater is the current. The *differential input* produces a current which depends upon the rate of change in the error signal, caused, for example, by setting the controller to a new temperature, or by a sudden draught. The currents output by the three units are summed, to provide an overall current which is sent to the heating element in the oven.

Procedure

The silica tube is already packed with charcoal and in place in the furnace - do not disturb it. If the soda-lime shows substantial purple coloration, ask the technician to show you how to change it. *It is important that the purple colour should not extend more than about half way down the tube when you are taking readings, otherwise significant amounts of carbon dioxide may pass through into the second bubble meter, and invalidate your measurements.*

Wear safety glasses in case a surge of gas should blow off one of the gas connections, check that the needle valve on the outlet of the cylinder regulator is shut, then turn on the main valve at the CO_2 cylinder - a positive pressure should be registered on the high pressure regulator gauge. Turn the pressure-adjusting handle on the regulator clockwise until a small positive pressure is indicated on the regulator output gauge, then open the needle valve on the regulator.

Cautiously open the tap on the bench from which gas can be fed into the apparatus, and set the flow rate, measured by the flow meter before the tube, to around 2; the exact rate is unimportant. The flow rate will change slightly as the temperature is raised, (the viscosity of gases is temperature-dependent, and varies with composition), so there is no point in trying to set the flow rate precisely.

Now check the flow rate using the left-hand bubble meter. Adjust the knob at the bottom of the flow meter before the charcoal tube, if necessary, to set a flow rate such that the film in the bubble meter neither moves so rapidly that it is hard to determine when a particular mark on the tube is passed, nor so slowly that it becomes tedious to take replicate measurements. In practice this means that a bubble takes about 20 - 60 seconds to move through the graduated section of the bubble meter.

Turn the tap by the flow meters so that exiting gas is directed to the exhaust pipe. If you do not do this, the soda-lime may be consumed by the time you are ready to take measurements, and you will then need to change it.

Switch on the furnace and controller using the mains switch at the right hand side of the controller. Press the SET button and dial in 600. Press the READ button on the controller to display the current temperature. When the temperature has stabilized, direct gas through the bubble meters and check the flow rate through the second is close to zero. At this temperature there should be little CO in the outflow from the furnace, so if the rate of gas flow through the second meter is significant, there is still some air left within the apparatus. Provided the amount of air is small, raise the temperature to 790°C.

When the temperature has stabilized, measure the flow rate of the gas emerging from the bed and of the residual gas after removing CO_2. Until the walls of the flow meters are wet, soap films within the tubes will burst, so send up films repeatedly until they reach the top without bursting. Only pass gas through the soda-lime bed when you wish to take a measurement, or the soda-lime will become exhausted.

Measure the rates of flow of (CO_2 + CO) and CO in the equilibrium mixture for at least six temperatures starting at 790°C. (Below 790°C equilibrium is attained too slowly for you to obtain meaningful results; above 900°C the equilibrium lies almost completely to the right.) At each temperature wait at least 10 minutes before taking readings, then take repeat readings until they become concordant (identical within experimental error.)

At the end of the experiment

(a) turn off the CO_2 supply at the bench tap and at the cylinder;
(b) turn off the PID controller.

Leave the two-way tap connected to the waste pipe, so that soap solution cannot be sucked back into the charcoal bed as the oven cools.

Calculation and discussion

Calculate the change in Gibbs Free Energy for the reaction using the "Third Law Method". To do this, locate values of standard entropy and enthalpy for the participants in the reaction. You can find these data in a variety of standard sources. From these data, calculate the value of the equilibrium constant at 25°C. Also, if possible, calculate the equilibrium constant at each of the temperatures for which you have experimental data. For this task you will need to use Kirchoff's equation and values for the heat capacities of reactants and products.

At each temperature, tabulate your flow rates and convert them into partial pressures of the two gases emerging from the furnace. (The partial pressures are proportional to the volumes of each gas, which in turn determine the rate at which the soap films move up the tubes.)

Calculate K_p at each temperature. Using the van't Hoff Isochore, construct a suitable graph, **including error bars**, from which to find the enthalpy of reaction.

Comment on your results, and on the magnitude and source of errors in the experiment, **showing clearly your estimate of error in your experimental value of enthalpy**. Comment on the agreement - or lack of it - between experiment and your third law values of K_p. In case of disagreement, consider what factors affect the values which you have used for the entropy and enthalpy of the participants in the reaction, and how reliable these values may be. Which of your experimental values would you expect to be most reliable? Which values would be most affected by any systematic errors you have identified in either the calculation or the experiment?

The incoming gas does not heat up instantly to the furnace temperature, nor does the gas emerging from the furnace cool instantly to room temperature. What effect might this have on the measured composition of the reaction mixture? What will be the effect on your results? Explain your arguments clearly.

Chemical Properties, Hazards and Emergency Treatment

Gloves are not necessary for this experiment, but may be worn if you wish. Neoprene or nitrile are both suitable materials.

Carbon Dioxide

Colourless odourless gas. Acts as an asphyxiant if present at high concentration. Exposure to dangerous levels is very unlikely in the open environment of the laboratory, but if a sudden large-scale release occurs, inform the demonstrator or technician and leave the laboratory.

Carbon monoxide

Colourless odourless gas. Highly toxic. Accumulates in the body and is only slowly removed from it. The experiment generates minor amounts of carbon monoxide which should be safely disposed of through the exhaust pipe. Do not attempt to repair the bubble meter if it is damaged in any way; instead shut off the flow of carbon dioxide and call for help from the technician.

Appendix A   Problems and Solutions

Observation	Indicates	Solution
Bubbles do not move up the bubble meter tube	No gas reaching bubble tube, or no soap film formed	(i) Check that the three-way tap at the bubble meter is correctly aligned. (ii) Turn on carbon dioxide cylinder and ensure gas is flowing through the meter at right of apparatus. (iii) Ask the technician to check for leaks. (iv) Condensed water is blocking the tube exiting from the oven - ask the technician to rectify. (v) Check that the quantity of soap solution in the teat is sufficient to form a film across the tube.
Bubbles move too quickly or slowly for precise measurement	Incorrect gas pressure	(i) Adjust gas pressure at right-hand flow meter
Little difference in flow rates through the two bubble meters	Carbon dioxide absorber exhausted, or equilibrium too far to the right	(i) If purple colour of soda lime absorber extends half way down the tube, replace absorber. (ii) If temperature is well above suggested limits, equilibrium mixture will be mainly CO - reduce the temperature (iii) Air remains in charcoal tube - continue working to allow carbon dioxide to flush out air.
Bubbles in tube break before reaching top	Tube not wet, bubble solution too weak	(i) Bubbles will break until the inside of the tube is wet - continue working. (ii) Prepare a stronger solution of the bubble mixture, add glycerol.
Calculated equilibrium constants are meaningless	Faulty experimental procedure, failure to perform correct calculation!	(i) Ensure that your calculation takes account of the fact that the volume of gas flowing up the first tube is the combined volume of carbon monoxide and carbon dioxide, while that flowing up the second tube is carbon monoxide alone. (ii) Check that your calculation uses partial pressures of gas, not flow times. (iii) Failure to change soda lime when purple colour extended more than half-way down tube.