

A JUNIOR YEAR CHE LABORATORY

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SOME EXPERIMENTS which the author ran in 1980-81 in the University of Edinburgh's third year chemical engineering laboratory are shown in Table 1. Fluid mechanics and thermodynamics laboratories are taken separately. This is the major chemical engineering formal lab, since the student does research and design projects in the fourth year of the course. The students work in pairs, starting at 10:00 a.m. and finishing nominally at 5:00 p.m. (in practice, between about 3:00 and 6:00 p.m.). The lab runs for two terms. In the third term of the session the weekly lab is omitted and there is a 'lab week' instead where the students devote the whole of one week to an open-ended short project, such as the development of a new lab experiment. This paper remarks on features of the experiments which might make them attractive for wider use.

CONVECTIVE MASS AND HEAT TRANSFER

Good convective mass transfer experiments are hard to find. This writer's experience with wetted wall columns, for instance, has not been happy. The purpose of this experiment is *not* the study of simultaneous heat and mass transfer, but the study *separately* of convective heat and mass transfer in the same geometry, to allow the j-factor analogy to be confirmed. The apparatus was originally a commercial heat transfer experiment, consisting of a 12.5 cm square duct with a perspex test section, through which air is drawn by a blower. Transverse rods of 1.25 cm diameter

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TABLE 1

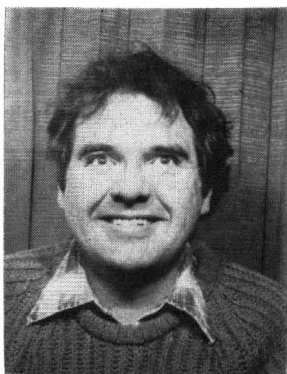
LIST OF EXPERIMENTS (1982)

Topic: Principal Measurement Method; Ancillary Equipment

1. Plate Heat Exchanger: Thermocouple
2. Film and Nucleate boiling: Thermocouple; Ammeter
3. Double Pipe Heat Exchanger: Thermocouple; Weigh Tank
4. Single Tube Condenser: Thermometer
5. Heat Transfer to a Jet: Liquid Crystal Sheet
6. Jacketed Pans: Thermometer; Weigh Tank
7. Process Control: Float; Micro-computer
8. Convective Mass and Heat Transfer: Balance, Thermocouple; Chart Recorder
9. Continuous Still: Densitometer
10. Continuous Liquid-Liquid Extraction: Titration
11. Drying: Continuous Weighing; Anemometer
12. Filtration: Volumetric Cylinder; Filter Leaf
13. Packed Tower Hydraulics: Manometer
14. Fluidised Beds: Manometer; Weigh Scales
15. Diffusion-Closed System: Gas Liquid Chromatography; Recorder and Integrator
16. Diffusion-open system: Katharometer; Chart Recorder
17. Measurement of Surface Area of Alumina: B.E.T. Apparatus; Liquid N₂
18. Packed Bed Catalytic Reactor: Gas Liquid Chromatography; Recorder and Integrator
19. Adiabatic Batch Reactor: Thermocouple; Micro-computer
20. Enzyme Catalysis: Polarimeter
21. C.S.T.R.: Spectrophotometer
22. Residence Time Distribution Study: Flame Ionisation Detector; Micro-computer
23. Coagulation: Pressure Transducer; Chart Recorder

are introduced through holes in the wall, to simulate up to four rows of a heat exchanger tube bank: all the rods but one are perspex dummies. The working rod is copper and has a thermocouple within it. This rod is heated electrically and then inserted into place at the start of the experiment. From its cooling curve the gas-rod heat transfer coefficient is deduced, and the experiment is repeated for different air velocities and test-rod positions. Measured pressure drops are also logged. Next, the mass transfer runs are performed.

The adaption to mass transfer work exploits



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Macleod's swollen polymer method [1, 2]. A thin film of commercial silicone rubber is deposited on the surface of the mass transfer working rod. This is swollen to equilibrium with some suitable volatile agent, *e.g.* ethyl salicylate. When the rod is placed in the air stream the agent evaporates. There is a constant rate drying period during which the partial pressure of the swelling agent immediately above the polymer is sensibly constant, equal to its saturated vapour pressure at the air temperature, and the controlling mass transfer resistance is rod-gas convection; diffusion through the polymer does not intrude. Intermittent withdrawal and weighing of the rod both establishes the mass transfer rate (and thus the mass transfer coefficient, for the partial pressure of swelling agent in the bulk gas is virtually zero) and confirms that the test is within the constant rate period. The rod can then be immersed in a test-tube of swelling agent for re-swelling to equilibrium, while a different test rod, ready prepared, is used for the next run. Since saturated vapour pressure is sensitive to temperature, it is important to measure the air temperature with more accuracy (*e.g.*, $\pm 0.1^\circ\text{C}$) than the heat transfer experiment requires.

The transfer coefficients are then nondimensionalised, to show that the restricted j factor analogy, $j_D = j_H$, holds, while the presence of form drag falsifies the complete j factor analogy $j_D = j_H = f/2$, where f is the friction factor. Alternative swelling agents, appropriate values of saturated vapour pressure and diffusivity, and other simple experiments using the swollen polymer

method are reported elsewhere [3, 4].

HEAT TRANSFER TO A JET

A flat horizontal sheet of plastic, of area A , incorporating a commercial liquid-crystal temperature-sensitive film, is heated from below by direct contact with an electric heating mat. The relation between sheet temperature and colour is established in preliminary experiments. The mat sits on insulating material so that all its power, W , measured as current times voltage, passes through the sheet. The sheet quickly reaches a thermal steady state, so that, in still air, it has a uniform colour. A round, laminar air jet is then aimed at the centre of the sheet, normal to its surface. Then, since the solid-air heat transfer

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coefficient, h , varies with position, r , so does the surface temperature of the film, T_s , and coloured rings appear on the film. The heat transfer coefficient, as a function of r , is calculated from

$$h(r) = W/A[T - T_s(r)]$$

and compared with theory [5]

$$\text{Nu}(r) = 0.159 \text{Pr}^{1/3} \text{Re}^{3/4} (d/r)^{5/4}$$

where d is the diameter of the jet.

The experiment is repeated with a square jet for which no theory exists, and the students explore the unexpected and interesting results. An improved and abbreviated (two hour) form of this experiment has been transplanted to the second-year fluid mechanics and transport processes lab in Cambridge. Details may be had by writing to Mr. N. MacFadyen.

DIFFUSION EXPERIMENTS

Usefully accurate gas diffusivity measurements can readily be made in a Stefan experiment [6] where evaporation rates are measured from a long-necked flask. However, this experiment does not involve the direct measurement of concentration profiles and is consequently found unsatisfactory by some students. The two experiments used in this lab are selected to remedy this defect, to show the difference between equimolecular counter-diffusion and diffusion through

a stagnant film, and to introduce the student to some moderately heavy mathematics and to some analytical instruments.

The counter-diffusion experiment is Gover's [7]. About 5 ml of, *e.g.*, acetone vapour is injected through a septum near the bottom of a vertical, lagged sealed glass tube (length *ca.* 60 cm, *i.d.* 2.5 cm) containing, as host gas, nitrogen traced with 3% ethane. A subsequent series of analyses of samples withdrawn (by 100 μ l gas-tight syringes) at two sample points each located at one-sixth of a tube length from an end permits determination of D_{AB} , the diffusivity of the vapour in nitrogen. The acetone concentration in counter-diffusion is described by the diffusion equation (Fick's second law)

$$\frac{\partial C_A}{\partial t} = D_{AB} \frac{\partial^2 C_A}{\partial Z^2}$$

$$\text{with } t = 0, \quad C_A(Z) = C_A^0(Z) \\ Z = 0, L, \quad \frac{\partial C_A}{\partial Z} = 0$$

where Z is the axial coordinate, t is time, and L is the tube length. The solution for $t > 0$ is obtained by separation of variables

$$C_A(Z,t) = A_0 + \sum_{k=1}^{\infty} A_k \exp\left(-\left(\frac{k\pi}{L}\right)^2 D_{AB}t\right) \cos \frac{k\pi Z}{L}$$

where the values of the coefficients $A_0 \dots A_{\infty}$ depend on the initial concentration $C_A^0(Z)$, that is, on the particular Z -wise concentration profile set up on completion of injection ($t = 0$).

Taking the difference of concentration between two points at the same time, the even terms cancel and the odd terms double. The location of the sample points causes the term in A_3 also to vanish, while the decaying exponential factor causes the terms in A_5 and higher to be negligible for all but the shortest times. Hence

$$[C_A(1/6 L, t) - C_A(5/6 L, t)]$$

is proportional to

$$\exp\left[-\frac{\pi^2}{L^2} D_{AB}t\right]$$

Thus the slope of a plot of the logarithm of that concentration difference against time yields D_{AB} . The unknown and unimportant A_1 is included in the intercept. Since a difference in vapour concentration is required, considerable error would result if the sample volumes were not identical. The purpose of the ethane tracer is to permit correction for differing sample volumes by use of the areas of the ethane peaks from the

GLC. Note that calibration of the GLC is unnecessary so long as peak area is proportional to the moles of species in the sample, since acetone peak areas (corrected using ethane peak areas) may be used in place of molar concentrations in the difference term above: the intercept of the plot changes, but not its slope.

The stagnant film experiment is Crosby's [8]. Here the film is arranged to be very thick—it occupies a diffusion cell about 0.4 m high. A pile of discs with a hole in each is assembled on a central pivot and can be arranged so that the holes are in line to form a vertical tube. At the bottom a reservoir carries a volatile liquid, *e.g.*, acetone. At the top a cap has a stream of nitrogen flowing through it. It is assumed that the concentration of vapour at the bottom is due to the vapour pressure at room temperature; at the top it is always zero. Starting with nitrogen only in the system, vapour is allowed access at zero time. At any subsequent time, t , vapour will have diffused towards the top. At time, t , alternate discs are rotated to isolate each section of the cell. A stream of nitrogen is used to flush out each section in turn and a quantity proportional to the vapour mole fraction is determined by a thermal conductivity cell (katharometer) attached to a chart recorder. The shape of the vapour concentration profile is thus established.

The only important modification from Crosby's design is that 'O'-rings were recessed into the horizontal faces of the dural discs to seal them adequately. The mathematics is laid out in BSL [9]. In contrast to the 'long time' analysis above, the analysis here is for 'short' times so that there is no breakthrough of acetone into the top cell. Then a semi-infinite boundary condition is used ($Z = \infty, C_A = 0$), and solution is effected by Boltzmann's transformation or by Laplace transform. The text is careful to draw attention to the error which could occur by naive application of Fick's second law. The measured value of diffusion coefficient may be compared with that from the experiment above.

ADIABATIC BATCH REACTOR

An exothermic batch reaction is performed batchwise in a stirred Dewar flask, with progress followed by measurement of temperature, as described by Williams [10]. However, in addition to the reactions he recommends (sodium thiosulfate with hydrogen peroxide, and acetic anhy-

drude hydrolysis), there is provision for study of the acid-catalysed hydrolysis of propylene oxide to the glycol [11]. Assuming that this reaction is pseudo zero order in H_2O , which is in great excess, and n^{th} order in propylene oxide, the heat and material balances yield the variation of temperature T with time t

$$\frac{1}{(T_f - T)^n} \frac{dT}{dt} = \left(\frac{C_o}{T_f - T_o} \right)^{n-1} A \exp(-E/RT)$$

where subscripts f and o imply final and initial. For an assumed value of n , the values of the pre-exponential factor, A , and the activation energy, E , may now be estimated either by (a) numerical/graphical differentiation of the measured T vs t curve followed by plotting the logarithm of the L.H.S. versus $1/T$ [10] or (b) by a numerical integration method [11] in which experimental errors tend to be cancelled rather than amplified. Both of these methods are readily programmed for the microcomputer which logs the T vs t curve (receiving a thermocouple signal amplified and digitised by a DVM). Also programmed is an ordinary differential equation (o.d.e.) integration routine which permits integration of the o.d.e. above with the estimated values of A and E and the assumed value of n . Thus the student can plot the predicted T vs t profile to compare with the experimental values, and choose the value of n (from, say, 0, $1/2$, 1, 2) which gives the best fit. It is also possible then to predict profiles for different initial concentrations (C_o) or temperatures (T_o), and so to find initial values which will lead to very different predictions of the profile for different assumed values of n . A second experiment allows easy discrimination of the best value of n [11].

A particular advantage of this reaction is that the order of reaction with respect to catalyst concentration, C_{H^+} , is easily found. From the o.d.e., writing $A'C_{H^+}^m$ for A ,

$$\begin{aligned} \int_{T_o}^{T_i} \frac{dT}{(T_f - T)^n \exp(-E/RT)} \\ &= \int_0^{t_i} \left(\frac{C_o}{T_f - T_o} \right)^{n-1} A'C_{H^+}^m dt \\ &= \left(\frac{C_o}{T_f - T_o} \right)^{n-1} A'C_{H^+}^m t_i \end{aligned}$$

Consider two runs using different values of C_{H^+} but the same initial values C_o , T_o , and hence the same final temperature T_f . Choose some convenient intermediate temperature T_i and note the corresponding values of t_i for the two runs. Now, the LHS is the same for *both* runs. So

$$(C_{H^+}^m t_i)$$

is constant too, so that the two pairs (C_{H^+}, t_i) immediately yield the value of m . As far as is known, this result is new. The values of n , m , E , A' obtained agree well with the literature [11, 12].

NOTES ON OTHER EXPERIMENTS

The packed tower hydraulics experiment is a conventional study of loading and flooding in two six-inch diameter towers, one packed with Raschig rings and the other with glass helices. However, it has one pleasing feature: the first tower floods first at the top, followed by the flooding moving downwards, whereas the second floods at the bottom and the flooded zone grows upwards. The cause of the former is presumably that the gas *volumetric* flow is highest at the top: of the latter, that the helices compress readily, so that the bed voidage is least at its base and resistance to flow is highest there. A remarkable number of students don't notice.

The packed bed catalytic reactor is used to study the dehydration of 2-propanol to a mixture of propylene and di (2-propyl) ether over an alumina catalyst: this reaction is only mildly endothermic so that reactor isothermality may be assumed, the reactor and the feed preheater being in an oven. Catalyst particles are so small that pore diffusion limitations do not occur.

The enzyme catalysis experiment is performed in a batch reactor made by modifying a spinning catalyst basket reactor of the Carberry type. Glucose is converted to fructose by an immobilised enzyme "sweetzyme Q" manufactured by Nova A. S. of Copenhagen, used at 60°C and $\text{pH} = 8.5$. The constants in the Michaelis-Menten kinetic expression are determined. The rotational speed of the basket can be varied from run to run to permit investigation of external mass transfer effects. \square

ACKNOWLEDGMENT

This lab was assembled as a team effort, so
Continued on page 160.

acidity, and shape selectivity are merged with a detailed evaluation of an intercrystalline surface mechanism to understand the product distribution and catalyst stability.

A thorough discussion is devoted to the ARGE fixed bed and fluidized bed SASOL processes for the direct conversion of syngas to fuels. Catalysts, reactor configurations, slides of the Sasol II Plant, surface reaction mechanistic models, Schulz-Flory kinetics and thermochemistry of syngas conversion to various products are parts of these lectures.

The lectures on the conversion of synthesis gas to chemicals is less oriented toward reactors and total processes; rather, they concentrate more on the detailed reaction mechanisms, using the pertinent coordination chemistry intermediates, to rationalize the conversion of syngas to various products. This is the first opportunity that the student has in the course to apply the fundamentals learned earlier to homogeneous and heterogeneous catalyzed processes. Some of the processes discussed are: acetic anhydride, acetic acid, ethylene glycol, vinyl acetate, and ethanol.

7. Technology of Major Advanced Chemical Processes

This section also concentrates on reaction mechanisms for both homogeneous and heterogeneous catalyzed processes. Aromatic side chain oxidation and butane oxidation to acetic acid are described by listing each of the proposed individual, elementary reactions required to form products. The coordination chemistry of the Wacker process, Carbide and Shell oxo-processes, Halcon propylene oxide process and others are illustrated. Likewise, the proposed surface mechanisms for the super basic zeolite catalyzed conversion of toluene and methanol to styrene and ZSM-5 zeolite catalysts for p-xylene production are explored along with several other.

8. Major Refining Processes

The principal processes utilized in a modern refinery are surveyed. A few of the processes like hydrodesulfurization are described in detail by way of an examination of the crystal chemistry of the catalyst, processing of various feedstocks, and reactor configuration. Most of the students' understanding of catalytic reforming, and catalytic cracking comes from assigned textbook reading. Several of the processes are viewed by 35 mm slides of various refinery units.

TERM PAPERS

Three term papers are assigned for the purpose of examining the details of several important areas of chemical and petroleum processing technology which are not covered in class. The emphasis in the papers is to provide a concise description of the major scientific and engineering aspects of the technology. In the past, Ziegler-Natta catalysis, catalytic cracking, and technology of heterogeneous, hydrocarbon partial oxidation were assigned.

EXAMS

Three one-hour exams are usually given which cover all material discussed in class. These exams are closed notes and books and are given soon after the subject matter is discussed in class. No comprehensive final has been given until now. Table 2 shows a typical exam, given in March of 1982. The high grade was 99, the low was 41, and the class average of 53 students was 70. □

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Continued from page 127.

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REFERENCES

1. Macleod, N., and R. B. Todd, *Int. J. Heat Mass Transfer*, 16, 485, 1973.
2. Kapur, D. N., and N. Macleod, *Ibid*, 17, 1151, 1974.
3. Paterson, W. R., R. A. Colledge, J. I. Macnab, J. A. Joy, to be submitted to *ibid*, 1985.
4. Paterson, W. R., A. K. Banerjee, N. P. Clark, D. C. Knott, N. P. Wooley, to be submitted 1985.
5. Scholtz, M. T. and O. Trass, *AIChE J*, 9, 548, 1963.
6. Bennett, C. O. and J. E. Myers, *Momentum, Heat and Mass Transfer*, 3rd ed., McGraw-Hill, Japan, p 516-7, 1982.
7. Gover, T. A., *J. Chem. Educ.*, 44, 409, 1967.
8. Crosby, E. J., *Experiments in Transport Phenomena*, Wiley, NY, p 139, 1965.
9. Bird, R. B., W. E. Stewart, E. N. Lightfoot, *Transport Phenomena*, Wiley, NY, p 594, 1960.
10. Williams, R. D., *Chem. Eng. Educ.*, Winter, 28, 1974.
11. Paterson, W. R. and D. L. Creswell, *Proc. 4th Int./6th Europ. Symp. Chem. Rn. Eng., Heidelberg*, p 121, 1976.
12. Creswell, D. L. and A. M. Santos, *Chem. Eng. Sci.*, 35, 283, 1980.