



University of Queensland

PAPERS

DEPARTMENT OF CHEMISTRY

VOLUME II

1953

NUMBER 1

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OF BENZOIC ACID

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M. E. R. PEAKE, M.Sc. APP.

Price : TWO SHILLINGS

THE UNIVERSITY OF QUEENSLAND PRESS
BRISBANE

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Registered at the General Post Office, Brisbane,
for transmission by Post as a Book.



Wholly set up and printed in Australia by
WATSON, FERGUSON AND COMPANY
Brisbane, Q.
1953

The Rate of Sublimation of Benzoic Acid

By M. E. R. PEAKE, M.Sc.App.

SYNOPSIS

The material presented in this paper represents the results of one of the few studies made on the sublimation of solids.

Experimental work was performed on the isothermal sublimation of pure, solid benzoic acid into dry air from the inside of a 16 mm. diameter glass tube. Runs were carried out over a range of Reynolds numbers from 4,000 to 10,000 at temperatures of 50°, 60°, and 70° C. The Schmidt group remained constant at 2.62.

Empirical equations derived were:

At 50° C.

$$k_G = 32.37 \times 10^{-6} (N_{Re})^{1.08}$$
$$j_M = 0.0065 (N_{Re})^{-0.05}$$

At 60°, 70° C.

$$k_G = 12.79 \times 10^{-6} (N_{Re})^{1.24}$$
$$j_M = 0.0023 (N_{Re})^{0.13}$$

The mass transfer coefficients showed no significant changes with variation of the temperature.

Little quantitative data have been published in connection with mass transfer rates from solids to gases. Fisher³ investigated the rate of sublimation of benzoic acid at temperatures of 25°, 35° and 45° C. and for Reynolds numbers from 87,000 to 379,000. He determined that the mass transfer coefficient varied directly with Reynolds number and also that it varied as $T^{-2.94}$ where T was the absolute temperature. Since runs were made at only three temperatures and comparatively low temperatures where the vapour pressure data are questionable (this was pointed out by Fisher) it was considered advisable to extend this work to higher temperatures, using Reynolds numbers from 4,000 to 10,000.

The author showed by dimensional analysis that the actual range of Reynolds numbers covered by Fisher was 1,450 to 6,317. According to generally accepted ideas on the flow of fluids, this would cause a variation in the motion of the fluid from viscous to turbulent; the critical Reynolds number in round pipes apparently never has a value less than about 2,100 and, in so far as experimental evidence is concerned, there seems to be no definite upper limit. Whether a single, unbroken curve could be used to correlate data in the two regions is a question which would involve careful consideration of problems in fluid dynamics.

Mass transfer in sublimation is a diffusional process and may be considered in the light of the two-film theory of Whitman.¹⁷ The experimental work involved in this paper consisted

of the isothermal sublimation of pure benzoic acid from an immobile surface coated on the inside of a tube through which air was passed. Thus concentration gradients on the solid side were eliminated and the major resistance to diffusion could be considered as being in the gas film. The problem was reduced, therefore, to a consideration of gas film coefficients and mass transfer factors based on resistances in the gas film.

There seems to be a dearth of information on the influence of temperature on the gas film coefficient. In studies on the absorption of sulphur dioxide in water, Whitney and Vivian¹⁸ stated that no conclusive evidence regarding the effect of temperature on the gas film coefficients has been presented although the available data indicate that the effect is probably minor. Fisher found that increasing temperature decreased the film coefficient. A further discussion on these effects will follow.

Several investigators have reported on mass transfer rates between gases and solid particles. Hurt⁷ measured rates of mass transfer for the following systems: adsorption of water vapour from air by various particles, adiabatic humidification of air, and the evaporation of naphthalene into air and into hydrogen. Gamson, Thodos and Hougen⁵, Wilke and Hougen¹⁹, Taecker and Hougen¹⁶ measured the rate of evaporation of water into a stream of air from wetted granules and packing during the constant rate drying period. Hobson and Thodos⁶ studied the vaporisation of water, n-butanol, toluene, n-octane and dodecane from the surfaces of spherical packings into air, nitrogen, carbon dioxide and hydrogen. Resnick and White¹⁵ investigated the rate at which naphthalene vaporised into air, hydrogen and carbon dioxide from fixed and fluidised beds. Gamson⁴ developed correlations to allow the transition from fixed to fluidised beds of solids.

Some attention has been paid also to mass transfer in solid-liquid systems. McCune and Wilhelm¹² reported on the dissolution of 2-naphthol in water from consolidated and from expanded fluidised beds. Mass transfer from solid, moulded shapes of benzoic acid, cinnamic acid and β -naphthol to water in streamline and turbulent flow was the subject of an investigation by Linton and Sherwood¹¹.

The present investigation was directed to a study of the effects of Reynolds number and of temperature on mass transfer in the isothermal sublimation of benzoic acid from a circular conduit to air flowing through it.

THEORY

Due to the low vapour pressures of benzoic acid at the temperatures considered, and the large amounts of air used as entrainer, simplifying assumptions may be made in calculating the driving forces in diffusion.

It is assumed that the driving force is a partial pressure difference across a gas film adjacent to the solid surface, and also that equilibrium conditions exist at the interface.

The rate at which mass is transferred within the gas phase is given by

$$N = k_G A (\Delta p)_m$$

The magnitude of the film coefficient is a function of the physical properties of the film as specified by the Schmidt number and the state of motion of the phase as defined by Reynolds number.

Mass transfer factors were introduced by Colburn² and Chilton and Colburn¹ to provide more stringent methods of correlating experimental data.

$$j = [k_G P_{gr} M_m / G] [\mu / \rho D_v]^{0.67}$$

j_M , the mass transfer factor, is dimensionless and independent of the system.

APPARATUS

The equipment used has many features in common with that used by Fisher.³

Compressed air was obtained by tapping the laboratory service line and was admitted to the apparatus through a $\frac{1}{4}$ " needle valve; water was removed from the air line by blowing through a drain valve. Control of the air flow was obtained after the needle valve by blowing off excess pressure under water.

Dry air was used throughout the experiments—to achieve this, the supply air was passed through a drying tower containing activated bauxite. This was reactivated when it had adsorbed one-tenth of its weight of water vapour.

Until run 22 the exit gas from the analytical train was sampled and passed through caustic soda scrubbers. Subsequently these analysers were not used; however, for the earlier runs it was necessary to remove carbon dioxide from the air stream. For this purpose a 2" diameter tower, 12" high, was packed with "ascarite" and placed after the drying tower.

Thus the air supplied to the diffusion tube was dry and free from carbon dioxide. Valves were arranged so that the towers could be by-passed when required.

Air flow rates were measured by passing the stream through an orifice assembly. This consisted of straight lengths of 2" standard pipe with a $\frac{1}{4}$ " diameter orifice plate clamped between standard pipe flanges; 34" of straight pipe preceded the plate and 14" followed it. Pressure tappings, made at distances D and $D/2$ from the plate (D = diameter of pipe in inches), led to a differential water manometer while the upstream tapping was also connected to an open tube mercury manometer. A mercury in glass thermometer, 0° to 50° C. (1/10° C.) measured the temperature of the air and was placed at the entrance to the 2" diameter pipe.

The air was heated by passing it through a 16 feet coil of $\frac{3}{8}$ " o.d. copper tubing (20 gauge) immersed in an oil bath. This bath contained filtered, used, crank-case oil and was fitted with a motor driven stirrer and a 1 kilowatt "Helicoil" oil immersion heater. The electrical energy supplied to this heater was controlled by a "Sunvic" bimetallic thermostat, T.S.1. A thermometer was suspended in the bath which was lagged externally with hair felt. The temperature of the heated air was measured by a mercury in glass thermometer, 40° to 120° C. (1/5° C.)—the depth of immersion was 3".

The diffusion tube itself consisted of a 5 feet length of 16 mm. pyrex glass tubing. This was coated inside with a layer of benzoic acid—the length of this layer was varied but

it was positioned so that there were always minimum calming section lengths of 16 cm. and 8 cm. preceding and following the coated section respectively; actually the calming lengths were always much greater than this. The tube was enclosed in an oil jacket consisting of 2" iron pipe lagged on the outside with $\frac{1}{2}$ " asbestos rope. The glass tube passed through rubber stoppers inserted in stuffing boxes situated in the centres of 2" standard pipe flanges. Crankcase oil was circulated through the annular space by means of a small gear pump driven by a $\frac{1}{4}$ H.P. single phase motor, 1,400 r.p.m.; the speed of the pump was reduced by a 6 to 1 pulley reduction drive. The oil was drawn from, and discharged back into, a reservoir lagged with hair felt. This contained a 1 kilowatt "Helicoil" oil immersion heater, the electrical input to this heater being governed by a "Sunvic" thermostat, T.S.3. Oil temperatures were measured by a mercury in glass thermometer, 40° to 120° C. (1/5° C.) placed at the exit from the oil jacket. Back pressures in the diffusion tube were indicated by a mercury manometer at the entrance to the tube. Since it was necessary to remove the diffusion tube at frequent intervals, provision for draining the oil jacket was made by placing a cock on the lower side of the pipe.

The analytical train consisted mainly of two freezing traps in series and two caustic soda scrubbers on the exit gas sample line. The two freezing traps for removing the benzoic acid from the exit gas were made of pyrex glass with B40 "Quickfit" ground glass joints—the air passed down a central tube to the base of the trap and left through a tube at the top of the outer jacket. The traps were about 9" deep and were immersed in "Thermos" flasks containing acetone to which solid carbon dioxide was added as a refrigerant. To prevent condensation of acid in the line leading from the diffusion tube to the first trap, nichrome resistance wire (27 S.W.G.) was wound around the asbestos covered line and an electrical potential applied across the wire; this potential was varied by means of a variable transformer—a "Voltrol." A bulb in the exit line from the second trap was packed with glass wool to remove any entrained acid. The air was then passed into a mixing bottle where the temperature was measured, and thence to the atmosphere. From this bottle a sample of gas was drawn by a small water ejector through two gas-washing bottles containing caustic soda solutions, a tube containing "ascarite" and a wet gas-meter (1/10 c. ft. per revolution or 1 c. ft./hr. maximum).

A valve suggested by Fisher was used in directing the air stream into the traps or to the atmosphere. This consisted of an eccentric wooden wheel which, on slight rotation in either direction, closed a rubber tube by pressing it against a fixed wooden strip. One of the rubber tubes was connected to a tee-piece in the line from the diffusion tube to the traps and the other to the exit line from the mixing bottle. The valve was kept in the required position by a small tension spring.

EXPERIMENTAL WORK

Coating the tube. A prime requisite was a uniform, reproducible coating of benzoic acid on the inside of the diffusion tube. The interior of the glass was first cleaned thoroughly with chromic acid solution, washed carefully and then wiped dry by pulling a cloth through the tube. Six inches of pure benzoic acid crystals (A.R. grade) were pushed towards the centre of the tube by a ram. The subliming tube, with both ends open, was placed on the sand bath and slowly heated over the length that was to be coated. When the acid melted,

the tube was lifted from the sand bath, placed on rollers and slightly tilted so that the acid flowed over the surface. The tube was rotated continuously as it cooled so that a uniform layer of interlacing, needle-like crystals formed on the wall. The coating was trimmed to the required length by immersing the tube vertically in a tall cylinder containing caustic soda solution. After the dissolution of unwanted benzoic acid the tube was removed and washed free from caustic soda by a well-directed jet of water and then dried. To remove any loosely adhering material, water was allowed to flow slowly through the tube; afterwards it was drained and allowed to dry.

Determination of apparent surface area of coating. This was performed by running into the tube measured volumes of water from a burette and noting the increase in level of water in the tube. From the average cross-sectional area thus ascertained an average internal diameter was calculated. Since the length of the deposit was measured the apparent surface area could be determined. The solubility of benzoic acid in water at 17° C. is only 0.2g. per 100g. of water¹⁴ and hence the tube could be filled with water with very little loss of acid.

Method of operation. Before a quantitative run could be carried out it was necessary to have steady the flow of air, its temperature and also the temperature of the benzoic acid in the diffusion tube. The pump, circulating oil through the jacket surrounding the diffusion tube, was started and the heater in the oil reservoir switched on. When the oil was at the desired temperature the thermostat and a three-heat switch in the circuit were adjusted so that the temperature was maintained within $\pm 0.5^\circ$ C. of the desired value. Meanwhile, the air was being heated to the same temperature as the subliming tube. During this period the exit tube from the air heating coil was disconnected from the diffusion tube to obviate unnecessary removal of benzoic acid from the wall. While the air was being heated the drying tower and, for the first set of runs, the "ascarite" tower were by-passed; the temperature of the exit air was held to within $\pm 0.5^\circ$ C. of the desired value.

The equipment following the diffusion tube was assembled and placed in position and the valve directing the air flow set so that air from the diffusion tube initially would pass through a tee-piece to the atmosphere. A voltage of from 15 to 45 volts was supplied to the winding of the exit line from the diffusion tube, depending on the air rate and its temperature. The acetone in the "Thermos" flasks containing the traps was cooled by the addition of solid carbon dioxide to a temperature less than -40° C.

When conditions of temperature and air-flow rate were uniform, the drying tower and "ascarite" tower were switched into the stream of air and then the exit line from the coil connected to the entrance to the subliming tube. The needle valve was adjusted to allow for the increased pressure drops and the air passed through the tube from 10 to 15 minutes to permit attainment of steady state conditions.

A quantitative run was commenced by turning the valve so that the air stream containing the benzoic acid was directed into the traps. At the same instant a stop watch was started to time the run. Benzoic acid condensed as a hard, adherent deposit on the walls of the trap. During the earlier runs a sample of the exit gas was drawn off through the caustic soda absorbers. Solid carbon dioxide was added to the acetone to keep the temperature at a low figure. The duration of most of the runs was from five minutes to one

minute, depending on the air rate and temperature. The amount of acid available for sublimation was limited by the nature of the equipment, and the runs were so spaced as to minimise recoatings of the tube. Also heat transfer rates in the condenser traps decreased as the deposit increased in thickness. These considerations were involved in determining the length of the run.

During the run the following observations were recorded—the inlet air temperature, the differential pressure across the orifice, the upstream pressure at the orifice, the temperature of the oil bath, the temperature of the hot air, the pressure at the entrance to the diffusion tube, the temperature of the oil in the oil jacket, the temperature of the exit air from the traps, the temperature at the gas meter. Atmospheric pressure was also noted.

The run was concluded by using the eccentric valve to redirect the air stream through the tee-piece to the atmosphere and the duration of the run determined from the stop watch. The needle valve was then closed and the heaters, stirrer and pump switched off.

Analysis. During actual test runs it was impossible to carry out material balances, but the freezing traps were shown to be quite effective by means of the following technique. The diffusion tube, without its coating of benzoic acid, was placed in position in the oil jacket and the remainder of the equipment assembled as for a test run. A layer of benzoic acid was made on the inside of a 6" length of pyrex glass tubing, the external diameter of which was very close to the internal diameter of the diffusion tube. After trimming and drying, the tube was weighed on a balance and then slid into the larger tube in the oil jacket. A run, No. 8 in the series, was done at 50° C., using an air rate of approximately 90 S.C.F./hr. The tube was re-weighed at the end of the run to determine the amount of acid sublimed. Of 0.0107 g. of acid sublimed, 0.0105 g. were recovered in the traps and absorbers—a recovery of about 98 per cent. w/w.

The method of determining the quantity of acid sublimed may now be noted. To each of the freezing traps 50 ml. of approximately 0.02 N. caustic soda solution were added from a burette which was supplied from a reservoir of carbonate-free solution, protected from atmospheric carbon dioxide by "ascarite" tubes. The dilute caustic soda was prepared from 15 N. solution which was separated from carbonate particles by centrifuging; the dilution was done with cool, freshly boiled distilled water. Each trap was shaken thoroughly to ensure complete dissolution of the benzoic acid, and the contents were then washed into a standard graduated 100 ml. flask and the volume adjusted. The 50 ml. of caustic soda solution added to the traps were always in excess of that required for reaction with the benzoic acid.

The amount of unreacted caustic soda was found by titrating 25 ml. aliquots of the solutions with a standard solution in water of potassium hydrogen phthalate using phenolphthalein as indicator. Until run 22 the quantity of caustic soda was determined by titration with hydrochloric acid using bromothymol blue as indicator. However, there was more scope for errors in this method, for the acid required standardisation against sodium carbonate. On the other hand, potassium hydrogen phthalate can be obtained in a very pure form and standard solutions can be prepared by dissolving the weighed amount in the requisite amount of distilled water; these solutions are quite stable.

The alkali solutions in the gas scrubbers were analysed in a similar fashion; the initial normality of the alkali used for the traps and absorbers was determined for every run in case there had been reaction with the glass container while in storage.

Duplicate determinations were made for each sample.

Vapour Pressure Relations.

Calculations were made using an equation initially proposed by Klosky, Woo and Flanigan⁹ and later quoted in tables of vapour pressure data,⁸ viz.:

$$\log P_v = 11.956 - (4409/T)$$

where T = temperature, absolute °K

P_v = vapour pressure of the solid, mm. mercury.

This equation is valid over the range 50°—121° C.

Errors.

The maximum possible error in estimating k_G was determined to be $\pm 42\%$ and for $j_M \pm 47\%$.

The most probable error was found to be $\pm 16\%$ for the mass transfer coefficient, k_G and $\pm 21\%$ for the mass transfer factor, j_M .

Data for Sublimers.

Run	Length of coated area —cm.	Average internal dia. of coating cm.	Apparent surface area —sq. ft.
9E—20E	69.3	1.49	0.349
21E—32E	38.7	1.66	0.218
33E—39E	32.4	1.61	0.177
40E—49E	48.5	1.58	0.259

Correlation of Data.

Theoretical considerations indicated that there should be a functional relationship between the mass transfer coefficient, k_G and Reynolds number, N_{Re} ; also, there should be a relation between the mass transfer factor, j_M and N_{Re} .

Data were correlated using the principle of least squares; for this purpose, the data were grouped into two sections—one comprised data at 50° C. and the other data at 60° and 70° C. Statistical tests, however, showed that it would not seem likely that the runs at 50° C. constituted a population different from that at 60° and 70° C. Moreover, at the runs at the lowest temperature, the analytical technique employed differed from that in subsequent runs and could account for a large part of the deviation; also, since the runs at the lowest

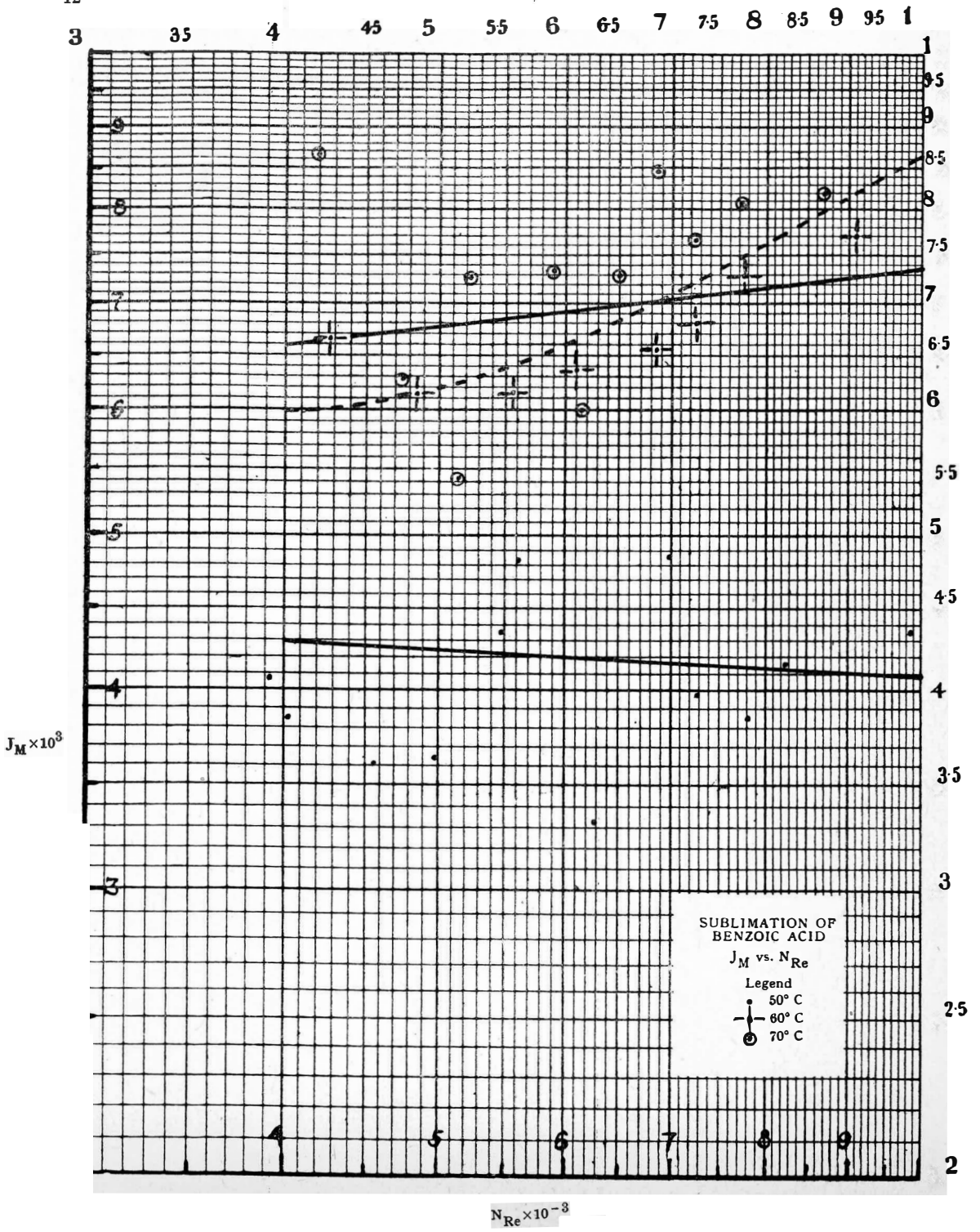
SUMMARY OF EXPERIMENTAL RESULTS

Run	Temp. °C.	Benzoic Acid $\times 10^{-6}$ lb. mol/hr.	Air lb. mol./hr.	p.p. acid $\times 10^{+5}$ atm.	$(\Delta p)_m$ $\times 10^5$ atm.	k_G lb. mol./ (hr.) (sq. ft.) (atm.)	G lb./ (sq. ft.) (hr.)	N_{Re}	N_{Sc}	j_M $\times 10^3$
9E	50	1.651	0.284	0.602	2.34	0.202	4370	4640	2.62	2.64
10E	50	2.605	0.383	0.732	2.27	0.330	5900	6280	2.62	3.32
11E	50	3.515	0.447	0.854	2.20	0.458	6900	7330	2.62	3.98
12E	50	4.025	0.507	0.880	2.18	0.529	7830	8240	2.62	4.17
13E	50	2.29	0.304	0.790	2.24	0.293	4690	4990	2.62	3.62
14E	50	1.975	0.243	0.835	2.21	0.256	3762	4010	2.62	3.86
15E	50	6.03	0.634	1.121	2.05	0.843	9760	10380	2.62	5.62
16E	50	2.92	0.334	0.922	2.17	0.386	5140	5470	2.62	4.35
17E	50	3.2	0.343	0.991	2.12	0.433	5270	5610	2.62	4.81
19E	50	6.1	0.60	1.149	2.70	0.648	9250	9840	2.62	4.38
20E	50	3.96	0.427	0.996	2.12	0.535	6590	7020	2.62	4.84
21E	70	6.70	0.186	3.66	14.72	0.209	2315	2635	2.62	5.07
22E (b)	70	16.2	0.294	5.74	13.55	0.548	3660	4160	2.62	8.61
23E	70	14.3	0.333	4.53	14.6	0.45	4150	4740	2.62	6.28
24E	70	13.3	0.366	3.88	14.6	0.418	4560	5170	2.62	5.41
25E	70	19.2	0.417	5.01	13.98	0.63	5180	5900	2.62	7.31
26E	70	16.85	0.434	4.25	14.35	0.538	5400	6150	2.62	6.00
27E	70	21.05	0.458	4.99	13.99	0.691	5710	6490	2.62	7.27
28E	70	24.85	0.485	5.64	13.61	0.837	6040	6875	2.62	8.41
29E	70	23.9	0.511	5.2	13.88	0.790	6350	7230	2.62	7.63
30E	70	26.45	0.547	5.43	13.73	0.884	6810	7750	2.62	8.05
31E	70	29.94	0.613	5.52	13.67	1.003	7640	8700	2.62	8.19
32E	70	17.27	0.367	5.0	13.95	0.568	4570	5210	2.62	7.28
34E	90	38.35	0.285	14.0	77.6	0.279	3775	3960	2.62	—
35E	90	35.4	0.286	12.9	78.25	0.255	3785	3980	2.62	—
36E	60	13.2	0.298	4.67	4.06	1.838	3940	4430	2.62	—
37E	60	9.79	0.285	3.65	4.78	1.158	3770	4250	2.62	—

SUMMARY OF EXPERIMENTAL RESULTS—Continued

Run	Temp. °C.	Benzoic Acid $\times 10^{-6}$ lb. mol/hr.	Air lb. mol./hr.	p.p. acid $\times 10^{-5}$ atm.	$(\Delta p)_m$ $\times 10^5$ atm.	k_G lb. mol./ (hr.) (sq. ft.) (atm.)	G lb./sq. ft.) (hr.)	N_{Re}	N_{Sc}	j_M $\times 10^3$
38E	60	11.09	0.30	3.86	4.64	1.35	3980	4480	2.62	—
39E	60	11.42	0.351	3.45	4.91	1.32	4640	5220	2.62	—
40E	60	6.81	0.318	2.23	5.65	0.466	4370	4825	2.62	6.13
41E	60	6.41	0.281	2.375	5.56	0.445	3850	4260	2.62	6.65
42E	60	7.63	0.366	2.29	5.61	0.525	5040	5560	2.62	6.15
43E	60	8.56	0.402	2.29	5.61	0.59	5530	6100	2.62	6.33
44E	60	9.68	0.45	2.35	5.58	0.67	6180	6830	2.62	6.53
45E	60	11.76	0.509	2.56	5.46	0.832	6990	7720	2.62	7.29
46E	60	13.90	0.596	2.68	5.39	0.996	8210	9075	2.62	7.71
47E	60	10.52	0.478	2.43	5.53	0.736	6590	7280	2.62	6.80
48E	50	2.66	0.505	0.59	2.36	0.436	6940	7820	2.62	3.85
49E	50	1.45	0.253	0.62	2.34	0.24	3475	3920	2.62	4.08

THE RATE OF SUBLIMATION OF BENZOIC ACID



temperature were usually of longer duration than those at the higher temperatures the possibility of loss of acid from the traps would be increased—it is possible that the sampling and analysing of the exit gas was not sensitive enough to detect small quantities of acid.

The following empirical equations were thus obtained:—

at 50° C.

$$k_G = 32.37 \times 10^{-6} (N_{Re})^{1.08}, \text{ with a correlation coefficient, } r = 0.975.$$

$$j_M = 0.0065 (N_{Re})^{-0.05} \text{ and } r = 0.041.$$

at 60° and 70° C.

$$k_G = 12.79 \times 10^{-6} (N_{Re})^{1.24} \text{ and } r = 0.965.$$

$$j_M = 0.0023 (N_{Re})^{0.13} \text{ and } r = 0.196.$$

The correlation coefficients for the j_M vs N_{Re} correlations seemed rather low for a straight line correlation. Now, r was calculated from the formula

$$r = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2\}}}$$

approximately, $j_M = Ck_G/N_{Re}$ where $C = \text{constant}$

$$\text{and } \log j_M = \log (Ck_G/N_{Re}).$$

If now $X = \log N_{Re}$ and $Y = \log k_G$ or $\log j_M$ as the case may be, the numerator for r was $\sum (XY) - \sum X \sum Y/n$.

The value of the denominator was not altered very much in the k_G and j_M correlations.

However, for the j_M correlation the magnitude of Y was algebraically ten times less than that for k_G and this reduced the value of r mainly by changes in the numerator. For small errors in N_{Re} a relatively larger deviation was obtained for j_M than for k_G .

Consideration of the Experimental Work.

It is felt that the nature of the surface at which sublimation occurs is of great importance in the study of this unit operation. The calculations performed contain an area term which was based on an apparent surface area of the coating. An examination of the coating showed it to be made up of a multitude of interlacing, needle-like crystals. A cross-section of the coated tube was made by filling a coated length of the glass tube with molten paraffin wax; after the wax solidified, a section was cut with a diamond wheel. The wax prevented shattering of the glass and deposit in the region of cutting; the wax was removed by steaming. Unfortunately, a residual film remained on the crystals and this masked the outline to some extent when they were examined under a microscope. To overcome this fault, ice, cooled to well below 0° C., was tried in place of the wax; however, this tended to melt on cutting and the crystals shattered in some cases. Sufficient was observed by this qualitative test to indicate that the actual area was very much larger than the apparent measured area.

Mass transfer data show an unfortunate tendency to scatter in graphical plots; this is due to the large experimental errors which often arise in calculating the mass transfer coefficients and j -factors.

In the majority of cases concerning mass transfer between phases it has been determined that k_G varies as $(N_{Re})^{0.83}$. Fisher came to the conclusion that k_G varied as $(N_{Re})^{1.0}$ in the case of sublimation; as shown at the beginning of this thesis the actual range covered by Fisher was Reynolds numbers 1450 to 6317. Still, this would not alter the slopes of plots of k_G vs N_{Re} on log-log paper, neglecting for the moment transition from streamline to turbulent motion; the graphs would be merely displaced in position. The power 0.83 on N_{Re} was obtained from experiments using wetted-wall towers; although some analogies may be drawn between the equipment as used both by the author and Fisher and wetted-wall columns it should not be inferred that the mechanisms of vaporisation, absorption, etc., and sublimation are necessarily the same.

With sublimation, surface conditions of the solid are particularly important. The idea of an amorphous surface layer whereby the mass transfer surface area would be increased enormously has been proposed.¹⁰ If such is the case, the true film coefficients are actually very much less than those reported. As mentioned in the section on theory, the resistances encountered in this case of sublimation reside in the gas film.

Linton and Sherwood¹¹ investigated mass transfer from solid shapes to water in streamline and turbulent flow and one of the systems used was the dissolution of benzoic acid from cast tubes into water. Since the j_M factors are independent of the system, the values obtained by the author should be capable of comparison with values obtained by Linton and Sherwood. The latter also examined the systems cinnamic acid—water, beta naphthol—water; they found that the data for beta naphthol were in good agreement with the Chilton-Colburn prediction as were the data for cinnamic acid at the higher Reynolds numbers. The values of j_M for benzoic acid were nearly threefold greater at high Reynolds numbers although the points for the three solutes fell together in the streamline region. On the whole their results are higher than those determined by the author. Linton and Sherwood reported difficulties in measuring the rate of solution of benzoic acid; they obtained a curve similar in shape to Nikuradse's friction curves.¹³ The author's results are intermediate in value between the values of Linton and Sherwood and those from the Chilton-Colburn correlation.

McCune and Wilhelm¹² and Hobson and Thodos⁶ extended the use of the j —factor concept to the liquid film for mass transfer between fluids and granular solids and showed that, for fixed beds, j_M for liquids and gases was identical.

They proposed the general empirical correlation for gases and liquids as:—

$$\log j_M = 0.7683 - 0.9175 \log (\text{modified } N_{Re}) + 0.0817 [\log (\text{modified } N_{Re})]^2$$

$$\text{where modified } N_{Re} = D_p G / \mu$$

D_p = equivalent particle diameter of the packing

G = superficial mass velocity of the fluid

μ = absolute viscosity of the fluid.

This generalised correlation was for fluids through granular solids and was really an extension of the flow of fluids through conduits—to use, however, the diameter of the duct instead of the equivalent particle diameter in the Reynolds number is not wholly justified, for, in the case of particles, factors depending on the bed porosity, the diameter of the particles,

the shape of the particles and their orientation and the roughness of the particles are involved in the calculation of friction factors and modified Reynolds number.

A comparison of some of the mass transfer factors is presented:

N_{Re}	Linton and Sherwood ¹¹	Hobson and Thodos ⁶	Author
3580	8.3	34.6	6.5
4950	10.6	31.1	6.8
6880	13.9	28.1	7.1
9900	11.6	25.5	7.4

Of the figures presented, Linton and Sherwood's figures are of the same order as the author's. Linton and Sherwood did not present an empirical equation connecting $\log j_M$ and $\log N_{Re}$ because of the scattering of their data. In the present investigation the author has indicated that a curved line relationship for j_M vs. N_{Re} on a log-log plot is possible.

Because of the rough surface of the acid coating it is expected that, in the region of the wall, eddy effects would be most marked—these eddies may have been propagated at right angles to the direction of fluid flow and may have disturbed the stagnant conditions usually accepted as being present in the film. Whitman's theory of a stagnant film is probably only partly true in this case; it seems that mass transfer by eddy diffusion is the controlling mechanism. With such turbulent conditions in the film and the main body of the fluid stream the variation of k_G with $(N_{Re})^{1.24}$ rather than $(N_{Re})^{0.83}$ is not entirely unexpected. Fisher came to the conclusion that k_G varied as $(N_{Re})^{1.0}$ in the case of sublimation.

The graph of j_M vs. N_{Re} on a log-log plot shows that j_M does not vary greatly with increasing Reynolds number—the correlation gives a variation with $(N_{Re})^{0.13}$.

The Chilton-Colburn correlation states that j_M varies as $(N_{Re})^{-0.2}$.

The high values obtained for benzoic acid may be due to irregular sublimation from the different facets of the acid coating—this would cause local irregularities in the intensities of the eddy patterns.

For the runs at 60°, 70° C., particularly, the points in the logarithmic plot of j_M vs. N_{Re} seem to show a sweep upwards with increasing Reynolds number—a curve has been dotted in to show this tendency. The shape of this curve is very similar to one obtained by Nikuradse¹³ for friction factors in roughened pipes; this is not unexpected for j —factors are essentially friction factors.

End effects were considered to be negligible. Linton and Sherwood¹¹ found in their studies on the dissolution of solids that the effect of tube length on the mass transfer factor

was negligible for a ratio of the tube length to diameter greater than six. The effect of tube length is particularly important in the streamline region. From the figures quoted in the table—Data for Sublimers—it can be seen that the lengths and areas of the coating were varied without noticeable effect on the correlations.

One of the objects of the investigation was to determine the influence of temperature on the rate of mass transfer. Whitney and Vivian¹⁸ found little variation in the gas film coefficient with temperature in the absorption of sulphur dioxide in water. In sublimation from a pure solid the gas film resistance is the chief resistance to diffusion; from graphical plots, it seems that, over the range of temperatures 50° to 70°, the film coefficient is not altered significantly by increase in temperature. The graphical plots presented by Fisher would seem to show little variation with temperature when experimental errors are considered.

ACKNOWLEDGMENTS

This investigation was carried out as Project 101 initially on a grant from the C.S.I.R.O. The work was performed in the Department of Chemistry, University of Queensland, under the direction of Associate Professor E. S. Edmiston, who suggested the project and whom the author thanks for his continual interest in the investigation. Thanks are due also to Mr. P. C. Brooks, of the Chemistry Department, who made some valuable suggestions.

NOMENCLATURE AND DIMENSIONS

A	= interfacial area across which diffusion occurs. sq. ft.
D_v	= diffusivity of vapour. sq. ft./hr.
G	= mass velocity. lb./(hr.) (sq. ft.).
j_M	= mass transfer factor.
k_G	= mass transfer coefficient, gas film. lb. moles/(hr.) (sq. ft.) (atm.).
M_m	= mean molecular weight of the gas.
N	= rate of mass transfer. lb. moles/hr.
N_{Sc}	= Schmidt number.
N_{Re}	= Reynolds number.
p_{gf}	= mean partial pressure of non-transferring component in the gas film, atm.
$(\Delta p)_m$	= logarithmic mean partial pressure difference, atm.
μ	= viscosity, absolute. lb./(hr.) (ft.)
ρ	= density. lb./c. ft.

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