Table II. Empirical Constants for the Pressure Drop Equation

$\Delta P = a(L-b)^c + d\,10^{eL}G$

Air–Calcium Chloride Solution System, 39 wt. % $CaCl_2$

ΔP = Differential pressure drop, inches water/ft. packing

L = Liquid mass flow rate, lb./sq. ft. hr.

G = Gas mass flow rate, lb./sq. ft. hr.

Packing Type	a	b	c	d	$e \times 10^5$
¼-inch Raschig rings	0.0926	1,780	0.601	0.01940	1.130
½-inch Raschig rings	0.00487	2,209	0.785	0.00673	0.866
½-inch Berl saddles	0.00286	2,333	0.807	0.00409	0.936
½-inch Intalox saddles	0.00135	2,253	0.896	0.00443	1.421
1-inch Raschig rings	0.0000396	7,046	1.000	0.00133	1.433
1-inch Intalox saddles	0.0000776	12,419	1.00	0.00243	0.436

coordinates. At these points, the constant liquid rate curves seemingly change the slope. Figure 8 is a comparison of the Δ P *vs.* G for ¼-inch Raschig rings plotted on arithmetical and also on logarithmic graphs. The nature of the data with a non zero intercept produces the askewed log-log curve, indicating, erroneously, the presence of more than one flow region.

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Material (Table I) supplementary to this article has been deposited as Document No. 7379 with the ADI auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to Chief, Photoduplication Service, Library of Congress.

Thermal Decomposition of Sodium Carbonate Solutions

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A high pressure autoclave was used to study the thermal decomposition of sodium carbonate to form sodium hydroxide in water solution. Solutions containing initially 1 wt. %, 2.5 wt. %, and 5 wt. % sodium carbonate were stripped with saturated steam at rates of 500 and 1000 ml./hr. Temperatures ranged from 410° F. to 594° F. at the corresponding equilibrium pressures. Conversion rate decreased as sodium carbonate concentration decreased at the same steaming rate and temperature. Rate of conversion also decreased as steaming rate was lowered. Higher temperatures resulted in higher absolute levels of conversion up to a maximum at 550° F. (1,000 p.s.i.g.) for 2.5 wt. % sodium carbonate solutions. Conversion of sodium carbonate to sodium hydroxide in water is limited by reaction equilibrium. Equilibrium data were obtained for the range of conditions studied.

PETROLEUM REFINERS are often faced with the problem of disposing of spent caustic solutions resulting from sweetening operations on petroleum fractions. Discard of such material into natural waters causes severe pollution problems and hence is subject to governmental restrictions. A particularly troublesome problem arises in disposing of caustic that has been used to wash some virgin and/or cracked distillates. A spent caustic from this type of operation contains naphthenic and phenolic compounds as well as sulfides and heavier mercaptans. The simple processes such as air blowing (*4*) or steam stripping are not applicable to spent caustic containing these materials. Because these compounds are difficult to remove, a complicated disposal process is needed.

Neutralization of the spent caustic with a weak acid, such as CO_2, will release the dissolved (or reacted) naphthenates and phenolates. Carbonation at atmospheric pressure converts sulfides to colloidal sulfur and sodium carbonate, and converts mercaptides, phenolates, and naphthenates to free organic compounds and sodium carbonate.

The organics separate from the carbonate solution and may be easily decanted. Such a process is applicable to most spent caustics.

There are two possible methods to convert the carbonate effluent from this process to reusable caustic. These are by lime treatment and thermal decomposition.

Treatment of carbonate with lime (CaO) forms caustic and precipitates calcium carbonate (*3*). Thermal decomposition moves the following equilibrium to the right (*6*):

$$Na_2CO_3 + H_2O \rightleftarrows 2NaOH + CO_2\uparrow \qquad (1)$$

At high temperatures the CO_2 can be stripped out, resulting in the formation of caustic. This process appears to be relatively simple. However, data were needed to establish the kinetics and equilibrium of the reaction in all concentration ranges. Some data were available (*2, 5*) at low concentrations. This article presents data at higher concentrations of sodium carbonate.

The carbonation step of the caustic regeneration process will actually result in a solution of $NaHCO_3$, ensuring that all of the contaminating organics have been removed. Thus, a series of reactions will take place in a recaustification process. First, the $NaHCO_3$ will decompose according to the reaction,

$$2NaHCO_3 \rightleftarrows Na_2CO_3 + H_2O + CO_2\uparrow \qquad (2)$$

Then, the carbonate will decompose further to form caustic according to Reaction 1.

These reactions will not occur simultaneously but will occur in series since the sodium bicarbonate and the sodium hydroxide cannot co-exist in solution. The decomposition of the bicarbonate proceeds very readily at elevated temperatures—i.e., Na_2CO_3 solution is used commercially to scrub CO_2 from gas mixtures and the $NaHCO_3$ solution formed is regenerated by simple boiling at atmospheric pressure (*1*). Since further decomposition of the carbonate to form caustic is more difficult, only this reaction has been studied.

EXPERIMENTAL PROCEDURE

The high pressure autoclave used to study the thermal conversion of sodium carbonate to caustic is shown in Figure 1. At the beginning of a run, 1500 ml. of a sodium carbonate solution are charged to the cold reactor. With reactor valves closed, electrical heating elements supply the heat necessary to raise the unit pressure to the desired operating level (this takes about 70 minutes for operation at 1500 p.s.i.g.). The magnetic agitator is also started at this time. The agitator has an up-down amplitude of 2 inches, and the vanes are arranged so that the top vane cuts the liquid surface during each oscillation, the lower one remaining submerged. The control valve on the overhead condenser is opened until the steaming rate, measured as condensed water collected in a graduate, is at the desired level. The pump is also started at this time to force distilled water from the blowcase through the heater and into the reactor. The heater in the water feed line is used to reduce the heat load on the boiler heating elements. Water enters the boiler through a porous metal disk located beneath the reciprocating agitator. The heat input to the unit is regulated by a rheostat on the line to the electrical heaters. This fixes the steaming rate at the set pressure. The unit is now operating "on condition." Continuous replacement of the water removed as steam ensures that the total sodium concentration in the reactor remains constant. It is usually necessary at the beginning of the run to adjust the pumping rate to balance the amounts of distilled water and steam. The distilled water used in these runs contains about 7 p.p.m. of dissolved CO_2.

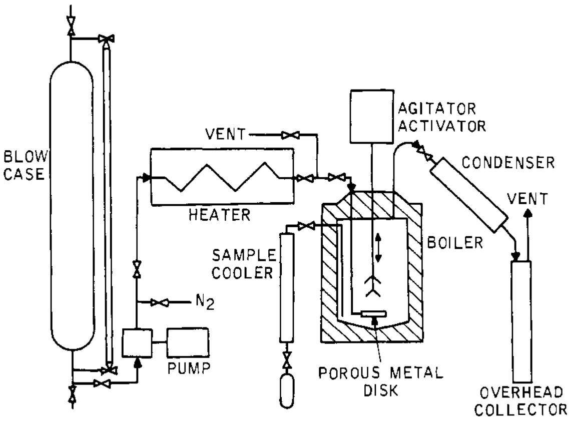

Figure 1. High-pressure stripping apparatus

Samples are withdrawn every hour. The 20-ml. samples are collected at unit pressure through the dip leg-condenser arrangement into an evacuated bomb. Two samples are taken each hour, the first to purge the sampling system, and the second to measure the progress of the reaction. The bomb is cooled before the pressure is released, and the contents transferred to a stoppered bottle.

Samples from runs made to study the thermal hydrolysis of sodium carbonate are analyzed for Na_2CO_3 and NaOH by potentiometric titration with 0.5N HCl. Such a procedure gives a titration curve with two breaks. The first break is the NaOH plus one sodium from the Na_2CO_3. The second break represents $NaHCO_3$. Results are reported as grams of NaOH and Na_2CO_3 per liter of solution. The conversion of carbonate is expressed as sodium carbonate and arranged in the ratio,

$$\text{Per Cent Conversion} = \frac{\text{NaOH (as } Na_2CO_3\text{)} \times 100}{\text{NaOH (as } Na_2CO_3\text{)} + Na_2CO_3}$$

The precision of the data obtained in this manner is good, as shown in Figure 2.

DISCUSSION

Data for the thermal decomposition of sodium carbonate solutions were obtained by stripping the CO_2 from Na_2CO_3 solutions at temperatures ranging from 410° to 596° F. and at corresponding pressures of 250 p.s.i.g. to 1400 p.s.i.g. These temperatures and pressures represent saturation conditions. Once pressure is specified, then the temperature will correspond to the equilibrium condition between boiling carbonate solution and its saturated vapor. Three liters of Na_2CO_3 solution ranging in concentration from 1.0% to 5.0% were stripped with 500 to 1500 ml./hr. of steam (measured as water at 77° F.). All percentage compositions are given on a weight basis.

Since the thermal hydrolysis reaction forms gaseous CO_2, stripping and contacting in the apparatus are of considerable interest. The data in Figure 2 also show the effect of contacting within the boiler. These data show that replacing the porous metal plate (conditions of "good" contacting) in the reactor by a simple dipleg (conditions of "poor" contacting) does not affect the carbonate conversion. Likewise, the addition of the make-up water at the reaction conditions (552° F.) has no effect on conversion. Apparently, the vibrations of the magnetic agitator provide sufficient mixing. The data in Table I show the effect of steaming rate (this is a measure of stripping) for various operating conditions at different concentration levels. These data show that the rate of removal of CO_2 from the reaction area is a definite limitation to the conversion of carbonate to caustic. A plot of the data is shown in Figure 3. All

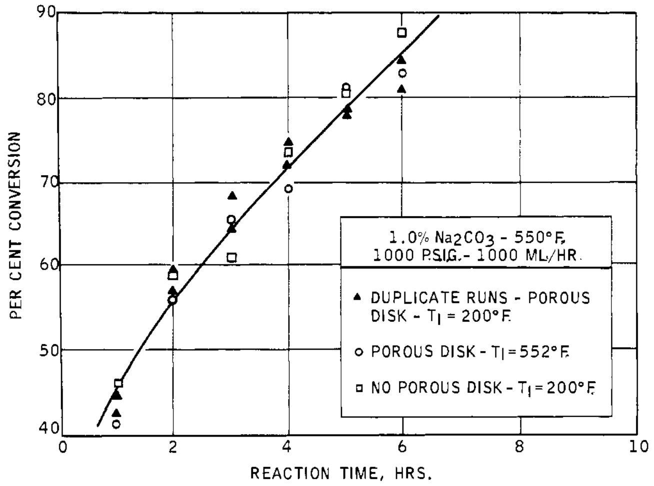

Figure 2. Precision of apparatus

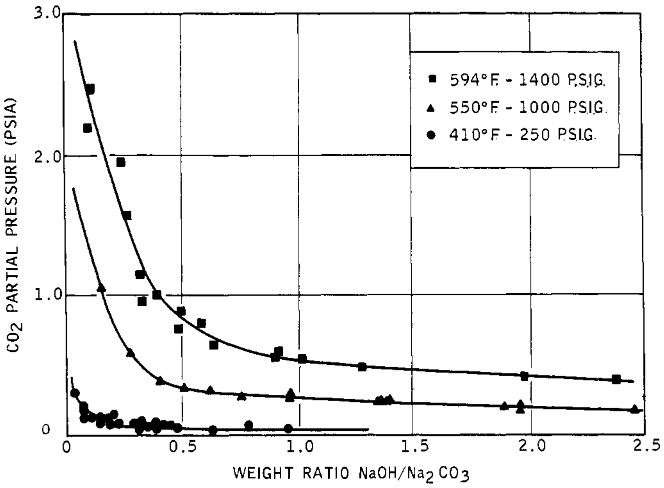

Figure 4. Partial pressure of carbon dioxide

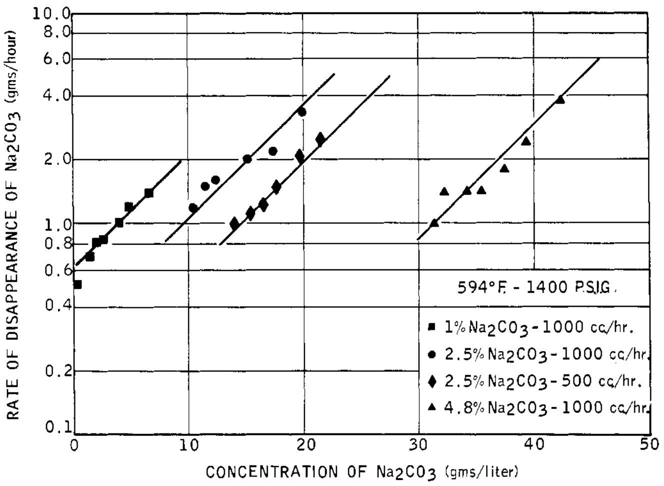

Figure 3. Carbonation rate *vs.* concentration

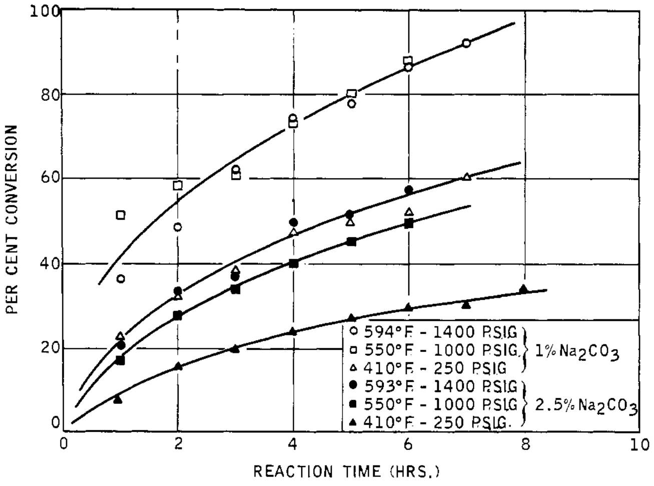

Figure 5. Effect of temperature and pressure

the lines are parallel for the different concentrations of Na_2CO_3. Higher initial carbonate concentrations result in an increased rate of conversion. The progress of the reaction reduces the concentration of carbonate with a resulting increase in the concentration of sodium hydroxide. Therefore, as the NaOH concentration increases, the rate of conversion decreases. Conversion rates at equal carbonate concentrations are not equal because, at these conditions, caustic concentration will be different depending upon the initial concentration of the solution. Conversion data for an initially 2.5% Na_2CO_3 solution shows that the rate of decomposition of carbonate doubles as the steam rate is doubled from 500 to 1000 ml./hr. at constant carbonate concentration.

Both observations in Figure 3 show that the conversion of carbonate to caustic is limited by reaction equilibrium. This can be further verified by plotting the variation of CO_2 partial pressure as a function of concentration, as in Figure 4. The concentration function chosen for this purpose was the ratio of caustic to carbonate. The use of such a measure of concentration eliminates effects caused by the existence of various caustic concentrations at equal carbonate concentration levels. The partial pressure is a

Table I. Effect of Steaming Rate on Conversion

Feed, % Na_2CO_3	2.4	0.97	2.5	4.8
Pressure, p.s.i.g.	1390	1400	1400	1400
Steaming rate, L./Hr.	0.47	0.80	0.95	0.93
Conc. of Na_2CO_3, G./L.				
After 1 hr.	21.5	6.0	20.0	42.3
2 hr.	19.5	4.9	17.5	39.3
3 hr.	17.7	3.8	15.2	37.4
4 hr.	16.5	2.8	13.5	35.5
5 hr.	15.3	2.0	11.7	34.1
6 hr.	14.0	1.3	10.5	32.2
7 hr.	...	0.7	...	31.2
Rate of Disappearance of Na_2CO_3, G./Hr.				
After 1 hr.	2.5	1.4	3.3	3.8
2 hr.	2.0	1.1	2.2	2.4
3 hr.	1.5	1.0	2.0	1.9
4 hr.	1.2	0.8	1.6	1.4
5 hr.	1.1	0.8	1.5	1.4
6 hr.	1.0	0.7	1.2	1.4
7 hr.	...	0.5	...	1.0

function of concentration and temperature (pressure) only. Even though these data include a threefold change in steaming rate, there is no steaming rate parameter. This is a condition of equilibrium.

Since carbon dioxide is formed in the hydrolysis of Na_2CO_3, equilibrium considerations indicate that increasing the pressure on the system would hinder the formation of NaOH. However, studies have shown that increasing the temperature increases the conversion. Since the system must be maintained in the liquid phase, high pressure is a necessary condition. Presumably, there may exist a temperature and pressure condition beyond which there can be no improvement in conversion. Such conditions actually do exist as is shown by the data in Figure 5. These data are for initially 1.0 and 2.5% Na_2CO_3 solutions and a steaming rate of 1000 ml./hr. and show that in most cases increases in temperature with the associated increases in pressure result in higher total conversion. However, for the 1% Na_2CO_3 solutions, while an increase in temperature from 410° to 550° F. and the resulting higher pressure improves the conversion considerably, further increase to 594° F. and 1000 p.s.i.g. results in no further advantage for the 1% Na_2CO_3 solutions.

Figure 5 also shows the effect of the initial concentration of carbonate on conversion at 593° F. and 1400 p.s.i.g. This is simply another means of looking at the data in Figure 3. Increasing the concentration from 1% to 2.5% equivalent Na_2CO_3 results in less than a twofold decrease in conversion. Conversion is not proportional to initial carbonate concentration because the NaOH concentration is different at different initial concentrations. As equivalent Na_2CO_3 concentration increases, conversion decreases in an exponential manner.

CONCLUSION

Equilibrium data for the thermal decomposition of concentrated sodium carbonate solutions have been obtained. Conversion of carbonate to caustic is limited by reaction equilibrium and depends on the volume of stripping gas. Optimum conditions exist, above which the increase in pressure associated with an increase in temperature inhibits further conversion.

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Thermal Conductivity of Porous Catalyst Pellets

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The effectiveness for reaction of the internal surface of a catalyst pellet depends upon the temperature and concentration profiles within the pellet. To evaluate the temperatures within pellets thermal conductivities must be known. Such information was measured by a comparative method for silver catalyst made by pelleting microporous powder particles. Data were obtained as a function of pellet density. The results showed very low conductivities [0.1 to 0.4 B.t.u./(hr. ft. ° F.)] in comparison with k_s for solid silver. Both micro and macro (spaces between powder particles) pores are shown to contribute to the low conductivity. Measurements as a function of pressure (1×10^{-2} – 760 mm. Hg.) suggest that free-molecule conduction is the primary mechanism of heat transfer in the micropores at pressures up to 760 mm. Hg. From these results it was estimated that the mean micropore size varied from 1500 to 5000 A. depending upon catalyst density.

IN 1955 Wheeler (*11*) estimated a temperature difference of 100° C. across the radius of an alumina catalyst pellet in an olefin hydrogenation reaction. Earlier Damkohler (*3*) had derived equations for estimating such temperature differences. Since then there has been considerable interest in the effect of temperature variations within the catalyst on the average rate of reaction for the pellet (*1, 2, 7*). The evaluation of the temperature profile depends upon the thermal conductivity of the porous material. Wheeler used a value of 0.24 B.t.u./(hr. ft. °F.) which meant that the catalyst pellet was an insulating material and explained the large temperature difference. The small amount of data that has become available confirms the insulating properties of porous catalysts. Hence, it is particularly important that accurate values of k_e be known to determine the potentially large temperature gradients and their corresponding effect on the average rate of reaction per pellet. The objective of this investigation was to measure thermal conductivities for silver (high conductivity solid phase) catalysts for comparison with data for other materials. Such published data appears to be limited to the investigations of Sehr (*10*) and Mischke (*8*) on pellets made from low-conductivity solids. The first study presented a comparison of methods of measurement and single values of k_e for five different catalysts. Mischke determined the effective thermal conductivity for several densities of alumina pellets under both vacuum and atmospheric pressure with helium and nitrogen.