# Vapor Pressure of Strong Sodium Hydroxide Solutions

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**The vapor pressure of water in sodium hydroxide solutions for three temperatures has been determined in the area of 0 to 0.8% water. The gas saturation method was used in this work.**

FOR THE evaporation of sodium hydroxide solutions in commercial practice, it is of importance to know the vapor pressure–temperature–water content relationship in the area of very small residual water—i.e., 0 to 0.8%. Although literature contains many references to determinations of the vapor pressure of sodium hydroxide solutions containing several per cent water and for temperatures below the melting point (322° C.), no data could be found for the desired area. This paper presents data obtained by the gas saturation method over the range 367° to 415° C. and 0 to 0.8% water in the molten caustic.

## EXPERIMENTAL

A commercial grade of ground sodium hydroxide analyzing 97.6% NaOH and about 2.4% total impurities on a dry basis ($Na_2CO_3$ 1.0; NaCl 0.4; $Na_2SO_4$ 0.3; $Na_2SiO_3$ 0.7) was used for this work. The sodium hydroxide container (Figure 1) 2⁷⁄₁₆ inches I. D. × 6 inches was made from 2½-inch IPS nickel pipe. The ⅜-inch head flange was fitted with a circular groove and asbestos gasket to seal it to the container. The stainless steel gas dispersion disk of 65-micron pore size and 2⅜-inch diameter was nickel plated before use. It reached to within ¼ inch of the bottom of the container. The flange top was fitted with two thermocouple wells made from ⅛-inch nickel pipe—one near the outside of the container and extending 5⁵⁄₁₆ inches below the top, the other near the center and reaching 4¼ inches below the top. A sodium hydroxide inlet point in the flange top was sealed with a ¾-inch plug. The container was heated in an electric furnace with high temperature insulation around the sides and top.

The nitrogen supply line incorporated a 1- × 10-inch ascarite column for $CO_2$ removal and a 2- × 20-inch dehydrite (drying) column and one low and one medium rate flow meter to give approximate rates.

Leading from the flange top, the metal portion of the ¼-inch gas outlet line was connected to a Hoke valve,

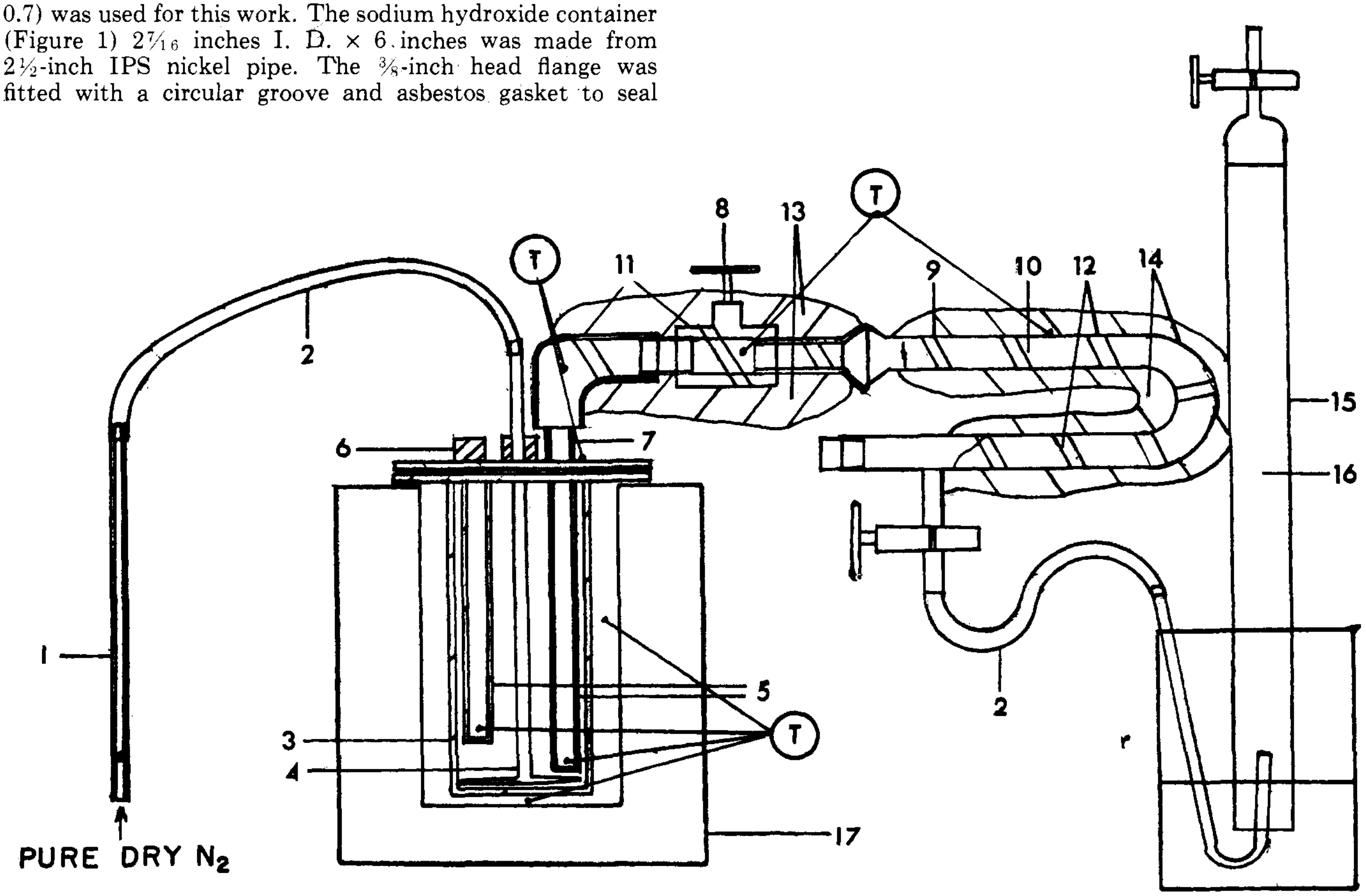

Figure 1. Schematic of vapor pressure apparatus

1. Flowmeter
2. Rubber tubing
3. NaOH container
4. Gas dispersing disk
5. Thermocouple wells
6. Inlet plug
7. Gas outlet
8. Valve
9. Glass U-tube
10. Drying agent, $Mg(ClO_4)_2$
11, 12. Heating tapes, 1 and 2
13, 14. Insulation, 1 and 2
15. Gas collecting cylinder
16. Shell Sol oil
17. Electric furnace
T. Thermocouple

followed by a ball joint at the end. The U-shaped glass absorption tube, containing the magnesium perchlorate drying agent, was about 6 inches long with a ball joint on one end to fit the metal one and a stopcock near the other end. The metal portion of the gas outlet line and most of the first leg of the glass tube were wound with heating tapes and asbestos insulation to maintain the temperature of the exiting gas above its dew point. Temperatures at eight points were recorded with the aid of thermocouples: two in the nickel container, top of flange, exit pipe elbow, Hoke valve, between absorption tube and heating tape, and two in the furnace. Dry gas exiting from the absorption tube was collected in a graduated cylinder (500 or 1000 cc.) over Shell Sol oil in order to obtain an accurate reading for the volume of nitrogen used. The vapor pressure of the oil at 25° C. was estimated to be 1 to 2 mm., which was neglected in the measured vapor pressures.

Since sodium hydroxide used in this work contained only 0.07% $H_2O$, it was necessary to add about 3 or 4 grams of water to the 500 to 600 grams of sodium hydroxide used in most runs to obtain the desired starting water content of about 0.8%. This was done after adding a portion of the charge to the container.

The nickel container with the flange cover in place was first pressurized and leak tested. After making all connections except the absorption tube, the container was heated at 300° C. or higher for several hours while passing nitrogen through it. In most cases, to obtain the depth of molten caustic desired, it was necessary to charge the container, melt the caustic, cool, and recharge, all under a small nitrogen flow. After remelting all the caustic, the valve was closed and the pot given a gentle swirling motion to obtain mixing of the caustic and water. Two absorption tubes were used alternatively, each change requiring removal of the heating tape, permitting the tube to cool to room temperature, disconnecting at the ball joint, carefully removing all grease and closing with a stopper before weighing. The other weighed tube then was placed in position and heated to about 120° C. During the change of tubes, the Hoke valve was closed. For each cycle step the nitrogen flow was usually regulated in the 50- to 100-cc. per minute range for a volume yielding usually 0.1 to 0.3 gram of water in the absorption tube. The volume of dry gas was then read together with the oil temperature and barometric pressure. In general, for total nitrogen volumes of less than 5000 cc., the run was interrupted each time the gas reservoir became full. This called for several fillings, the sum of which gave the total volume of dry nitrogen. In the few instances where volumes of nitrogen in excess of 5000 cc. were needed (such as steps 19 and 20 for the 367° C. run), the total volume in each case was obtained from the time and flow rate, the latter given by a measured volume collected in the reservoir.

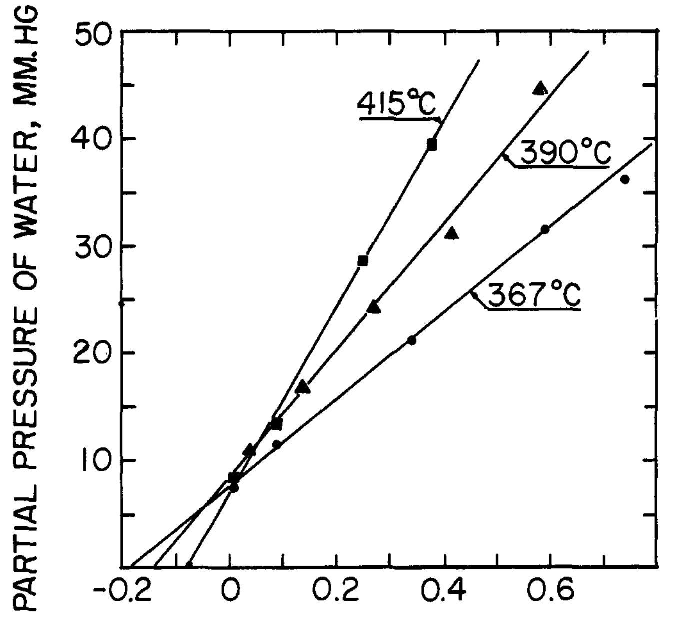

Figure 2. Determination of water left in caustic

## RESULTS

Vapor pressure data were obtained for three fixed temperatures, 367°, 390°, and 415° C. The vapor pressure, $p_{H_2O}$ in millimeters of Hg, for each step may be calculated from the equations

$$V_{H_2O} = (g/M)RT'/p_1 \tag{1}$$

$$p_{H_2O} = (V_{H_2O}/V) \times p_2 \tag{2}$$

Since it would take a long time and large volumes of nitrogen to eliminate the last traces of water from the caustic, this remaining water was determined by an extrapolation method (Figure 2). The method of calculating the weight and per cent of water in the caustic for each vapor pressure will be illustrated using the data for the 367° C. run. This run consisted of 21 steps, data for the last five being listed in reverse order in Table I.

$X$ represents the weight of water remaining in the caustic after performing step 21. The average water content of the caustic while actually performing this step to obtain the $p_{H_2O}$ value then was the water content at the end of this step plus one-half that removed, namely $x + (0.0146/2) = x + 0.0073$ grams. Similarly for step 20 the average water content was $x + 0.0146 + (0.1566/2) = x + 0.0929$ grams. Plotting the $p_{H_2O}$ values in column 9 against the numerical data of column 10 a straight line results (Figure 2). The value of $x$ can be read graphically as $-0.175$ grams following which the data for the last two columns in Table I can be readily calculated.

The complete data for all three temperatures are shown in Table II and Figure 3. Table III and Figure 4 show data for duplicate runs at 367° C. These data include the nitrogen flow rates used for each step.

Table I. Water Remaining in Caustic[a]

| Step No. | $V_{N_2}$, Cc. | $N_2$ Flow, Cc./Min. | Temp., ° C. | $p_2$, Mm. of Hg | Wt. $H_2O$, G. | $V_{H_2O}$, Cc. | $V_{H_2O} + V_{N_2}$, Cc. | $p_{H_2O}$, Mm. of Hg | Total $H_2O$ Left in Caustic, G. | | $H_2O$, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 21 | 1,990 | 83 | 29 | 754 | 0.0146 | 20.2 | 2010.3 | 7.6 | $x + 0.0073$[b] | 0.1823 | 0.031 |
| 20 | 14,000 | 75 | 28 | 754 | 0.1566 | 216.4 | 14216.4 | 11.5 | $x + 0.0929$ | 0.2679 | 0.045 |
| 19 | 16,000 | 75 | 27 | 754 | 0.3378 | 466.0 | 16466.0 | 21.3 | $x + 0.3401$ | 0.5151 | 0.087 |
| 18 | 4,991 | 71 | 28 | 755 | 0.1584 | 218.3 | 5209.5 | 31.6 | $x + 0.5882$ | 0.7623 | 0.129 |
| 17 | 3,986 | 63 | 28 | 755 | 0.1458 | 201.2 | 4187.2 | 36.3 | $x + 0.7403$ | 0.9153 | 0.155 |

[a] Weight of dry caustic = 590 grams. [b] $x$ represents the weight of water remaining in the caustic after performing step 21.

Table II. Vapor Pressure vs. Per Cent of $H_2O$ in NaOH

| | | | |
|---|---|---|---|
| Temperature, ° C. | 367 | 390 | 415 |
| Weight of dry NaOH, g. | 590 | 486.7 | 503.5 |
| Molten NaOH depth, in. | 4 1/2 | 3 3/4 | 3 3/4 |
| $N_2$ flow rate, cc./min. | 17-90 | 45-103 | 48-101 |

| | Run 1 | | Run 2 | | Run 3 | |
|---|---|---|---|---|---|---|
| Step No. | $p_{H_2O}$ | $H_2O$, % | $p_{H_2O}$ | $H_2O$, % | $p_{H_2O}$ | $H_2O$, % |
| 1 | 147 | 0.528 | 339 | 0.830 | 447 | 0.774 |
| 2 | 136.7 | 0.500 | 325 | 0.772 | 397 | 0.715 |
| 3 | 127.1 | 0.474 | 283 | 0.720 | 375 | 0.660 |
| 4 | 123.0 | 0.450 | 257 | 0.678 | 343 | 0.607 |
| 5 | 117.7 | 0.426 | 238 | 0.640 | 305 | 0.558 |
| 6 | 110.7 | 0.404 | 229 | 0.607 | 279 | 0.513 |
| 7 | 100.6 | 0.386 | 207 | 0.565 | 256 | 0.473 |
| 8 | 99.7 | 0.366 | 198 | 0.532 | 228 | 0.438 |
| 9 | 92.3 | 0.347 | 178 | 0.496 | 205 | 0.402 |
| 10 | 84.8 | 0.321 | 164 | 0.466 | 181 | 0.362 |
| 11 | 80.8 | 0.316 | 150 | 0.433 | 160 | 0.324 |
| 12 | 75.8 | 0.295 | 142 | 0.397 | 141 | 0.289 |
| 13 | 67.1 | 0.269 | 127 | 0.364 | 124 | 0.258 |
| 14 | 60.4 | 0.241 | 115 | 0.346 | 113 | 0.231 |
| 15 | 52.0 | 0.212 | 106 | 0.310 | 98.8 | 0.207 |
| 16 | 44.7 | 0.183 | 93.6 | 0.287 | 83.0 | 0.179 |
| 17 | 36.3 | 0.155 | 85.6 | 0.257 | 69.5 | 0.147 |
| 18 | 31.6 | 0.129 | 72.6 | 0.222 | 50.9 | 0.117 |
| 19 | 21.3 | 0.087 | 59.7 | 0.187 | 39.5 | 0.089 |
| 20 | 11.5 | 0.045 | 44.6 | 0.149 | 28.6 | 0.063 |
| 21 | 7.6 | 0.031 | 31.1 | 0.114 | 13.7 | 0.033 |
| 22 | | | 24.0 | 0.083 | 8.3 | 0.016 |
| 23 | | | 16.7 | 0.058 | | |
| 24 | | | 10.6 | 0.037 | | |

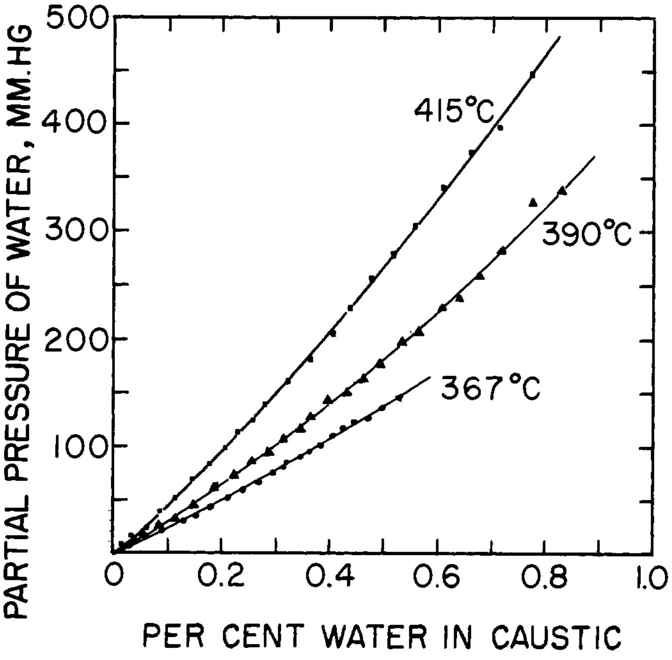

Figure 3. Vapor pressure of water in caustic at 367°, 390°, and 415° C.

## DISCUSSION

Frequent tests for alkalinity in the absorption tube indicated no vaporization or mechanical carry-over of caustic at the temperatures and gas flow rates used. All the water collected in the absorption tube was assumed to be free water in the caustic and none from the reaction: $2NaOH \rightarrow Na_2O + H_2O$. The work of Kay and Gregory (*1*), who found the vapor pressure of water at 300° C. from this reaction to be about $10^{-8}$ atm., supports this assumption. Extrapolating their data to 400° C., a vapor pressure of about 0.01 mm. was obtained. Thus at zero water content in the caustic the vapor pressure must be essentially zero, thus justifying the author's extrapolation to zero vapor pressure to obtain a measure of the water remaining in the caustic at the end of each run.

Because of the gas space above the molten caustic in the container and that in the exit line, the water content of the caustic does not correspond exactly to the vapor pressure for any given step. In the most extreme case, this gas space was estimated to be about 180 cc. at an average temperature of about 300° C. corresponding to 90 cc. at 25° C. The smallest combined volume of $N_2$ + $H_2O$ in a few steps was about 700 cc. and in most cases much greater. In view of this, the pairs of values in each step were considered to be close enough to make any correction unnecessary.

Practically identical temperatures were recorded by the two thermocouples located at two different points in the caustic. Upon turning the flow of nitrogen on or off, little or no temperature change was observed. Since the gas must provide some mixing action, this was taken as evidence that the molten caustic maintained a reasonably uniform temperature.

Considerable effort was directed toward demonstrating the attainment of equilibrium by the nitrogen gas as it passed thru the caustic. To obtain accurate vapor pressure values, the gas must become heated to the temperature of the caustic and also absorb water from the caustic to give the appropriate equilibrium vapor pressure. The following point is offered as proof that this equilibrium was actually realized.

In the duplicate runs, made at 367° C. using consistently higher gas flow rates in run 2 relative to 1, good agreement was obtained (Figure 4 and Table III). This is especially true for vapor pressures below 90 mm. In this area the nitrogen flow rates in run 1 varied from 27 to 83 cc. per minute; in run 2 from 80 to 133 cc. per minute. One

Table III. Vapor Pressure vs. $N_2$ Flow Rate

| | | | | | | |
|---|---|---|---|---|---|---|
| Temperature, °C. | | 367 | | | 367 | |
| Weight of dry NaOH, g. | | 590 | | | 522 | |
| Molten NaOH depth, in. | | 4 1/2 | | | 4 | |
| | | Run 1 | | | Run 2 | |
| Step No. | $N_2$ flow rate, cc./min. | $p_{H_2O}$ | $H_2O$, % | $N_2$ flow rate, cc./min. | $p_{H_2O}$ | $H_2O$, % |
| 1 | 50 | 147 | 0.528 | 68 | 166 | 0.632 |
| 2 | 17 | 136.7 | 0.500 | 67 | 156 | 0.595 |
| 3 | 90 | 127.1 | 0.474 | 91 | 156 | 0.558 |
| 4 | 45 | 123.0 | 0.450 | 96 | 138 | 0.525 |
| 5 | 48 | 117.7 | 0.426 | 102 | 128 | 0.495 |
| 6 | 55 | 110.7 | 0.404 | 105 | 119 | 0.468 |
| 7 | 52 | 100.6 | 0.386 | 97 | 121 | 0.440 |
| 8 | 60 | 99.7 | 0.366 | 102 | 116 | 0.414 |
| 9 | . . | 92.3 | 0.347 | 103 | 107 | 0.390 |
| 10 | 27 | 84.8 | 0.321 | 110 | 93.5 | 0.369 |
| 11 | 55 | 80.8 | 0.316 | 133 | 88.8 | 0.350 |
| 12 | 57 | 75.8 | 0.295 | 80 | 84.0 | 0.323 |
| 13 | 50 | 67.1 | 0.269 | 110 | 72.8 | 0.291 |
| 14 | 54 | 60.4 | 0.241 | 104 | 66.4 | 0.262 |
| 15 | 60 | 52.0 | 0.212 | 108 | 59.8 | 0.235 |
| 16 | 60 | 44.7 | 0.183 | 111 | 52.0 | 0.209 |
| 17 | 63 | 36.3 | 0.155 | 107 | 44.5 | 0.181 |
| 18 | 71 | 31.6 | 0.129 | 100 | 39.1 | 0.153 |
| 19 | 75 | 21.3 | 0.087 | 100 | 30.4 | 0.123 |
| 20 | 75 | 11.5 | 0.045 | 100 | 24.6 | 0.098 |
| 21 | 83 | 7.6 | 0.031 | | | |

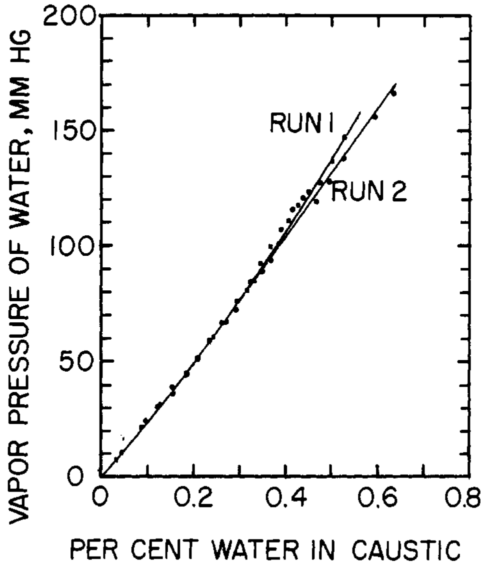

Figure 4. Vapor pressure of water in duplicate runs at 367° C.

must conclude that all gas bubbles, regardless of size, attained equal temperatures and equal moisture contents—i.e., the temperature of the molten caustic and the moisture content equal to the vapor pressure at 367° C. or the partial vapor pressure of the water above the surface of the caustic.

Since the volume of nitrogen gas passed through the molten caustic in each step is measured at room temperature, the weight of water collected can be converted to its corresponding hypothetical volume at this same temperature using the gas law Equation 1. The partial pressure of the water can then be calculated using Equation 2 where $V_{H_2O}/V$ is equivalent to the mole fraction of the water vapor.

Alternatively, the volume of the two gases could have been found at the temperature of the molten caustic, but this is not necessary since the temperature factor is common, and hence the ratio $V_{H_2O}/V$ remains the same.

Ideal gas behavior has been assumed in this work, and this seems justified at the high temperatures and low vapor pressures.

## NOMENCLATURE

$V_{H_2O}$ = volume of water as vapor in cubic centimeters calculated for room temperature and barometric pressure
$p_{H_2O}$ = partial vapor pressure of water in mm. of Hg
$V$ = $V_{H_2O} + V_{N_2}$ at room temperature
$p_1$ = barometric pressure in atmospheres
$p_2$ = barometric pressure in mm. of Hg
$g$ = weight of water for a single step in grams
$M$ = molecular weight of water in grams
$R$ = gas constant, 82.057 cc. atm.
$T$ = absolute temperature,° K.

## LITERATURE CITED

(1) Kay, E., Gregory, N.W., *J. Am. Chem. Soc.* **80**, 5648 (1958).

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