Solubility of Lithium Hydroxide in Water and Vapor Pressure of Solutions above 220° F.

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LITHIUM HYDROXIDE is being used as an agent for the control of pH in the primary coolant-water circuits of pressurized nuclear reactors. Basic information on the properties of lithium hydroxide solutions at elevated temperatures is important. For example, both corrosion and heat transfer are related to a buildup of concentrated films of crystalline deposits. Solubility data, therefore, are necessary to help predict the possibility of deposit formation from additions of lithium hydroxide. Similarly, vapor-pressure data help to establish the conditions under which concentrated films might occur at steam-blanketed areas. The present study was made to furnish data in each of the areas just mentioned.

APPARATUS AND EXPERIMENTAL PROCEDURES

The apparatus for obtaining the solubility data is schematically shown in Figure 1. The reaction vessel (*A*) was a standard American Instrument Co. Type 347 stainless steel autoclave with a drop-in nickel liner. The liner, having a capacity of 700 ml., was made of welded nickel sheet. The reaction vessel and heater were rocked 30° from the vertical at ten strokes per minute to agitate the solutions. Two openings for ¼-inch, high-pressure fittings were placed in the head. One opening was fitted for measuring pressures and for evacuating; the other opening was fitted for sampling the supernatant liquid in the chamber. The line leading directly from the head of the autoclave included a valve (V_2) for bleedoff, or evacuation, and a shutoff valve (V_3). This line led through a spiral to a Crosby Steam Gage Co. Model CD2 dead-weight gage tester (G_1) for measuring the pressure on the system. The condensed vapor from the autoclave was separated from the oil in the gage by a mercury bridge (*M*). This line also included a 5000-p.s.i. Bourdon-type gage (G_2) and a safety head with a 4200-p.s.i. rupture disk (*SH*). The outlet from the safety head led into a 1-liter pressure vessel (*PV*) which would contain the solution, should the temperature or pressure get out of control.

Samples of the liquid were drawn through a pressure tubing line extending through the head of the autoclave down two-thirds of the way into the chamber. A small stainless steel frit (F_1), having a 5-micron rated opening, was inserted in the end of this tube to filter the supernatant liquid. The sampling tube leading from the autoclave head contained a three-way, Y-type pressure valve (V_1). This valve was heated by two small plate heaters. Another small stainless steel frit (F_2) was inserted in the sampling line just ahead of the valve (V_1). This valve permitted attachment of two sample receivers (*SA*) at the same time.

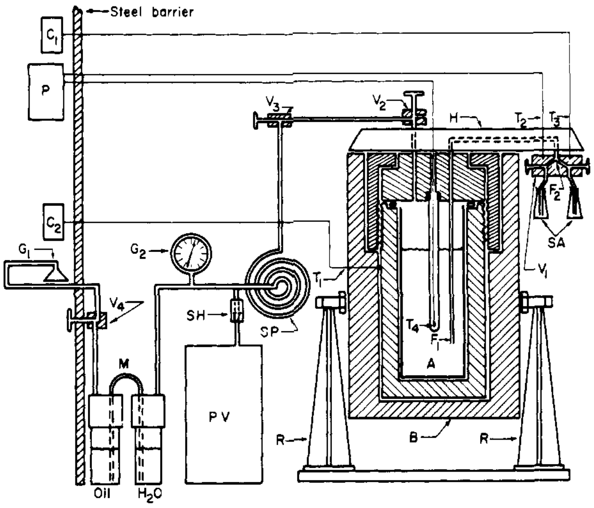


Figure 1. Apparatus for solubility and vapor pressure studies at elevated temperatures

A. 840-ml. autoclave with a drop-in nickel liner
B. Autoclave heater
C_1, C_2. Foxboro controllers
F_1, F_2. Stainless steel filter
G_1. Crosby Steam Gage Co., dead-weight gage tester, Model CD2
G_2. Bourdon tube gage
H. Heating mantle
M. Mercury bridge
P. Leeds and Northrup semiprecision potentiometer
PV. 1-liter pressure vessel
SA. Sample receivers
SP. Spiral tube
SH. Safety head
T_1, T_2, T_3, T_4. Thermocouples
V_1, V_2, V_3, V_4. Pressure valves
R. Rocker autoclave support

Lithium hydroxide monohydrate, reagent grade, containing 2.2 weight % lithium carbonate, was used as a starting material. A quantity of the solid reagent was stirred in distilled water for 10 minutes, allowed to settle, and the supernatant liquid was decanted into a polyethylene bottle. This solution (containing about 10 grams of LiOH per 100 grams of water) was run into a measuring buret and then through a column containing Rohm and Haas Amerlite XE154 lithium-form, ion-exchange resin to remove the carbonate. All vents in the solution line were fitted with tubes containing Ascarite to reduce CO_2 contamination. Carbonate could not be detected in the solution from the ion-exchange column by a double indicator titration.

The assembled autoclave was evacuated, and 500 ml. of the lithium hydroxide solution was drawn directly from the ion-exchange column through the sampling valve into the cold autoclave. The solution was heated to 250° F. and concentrated by allowing 400 ml. of condensed water vapor to escape through the valve (V_2). The autoclave was then cooled, 400 ml. of solution was drawn in, the autoclave was reheated, and the water was evaporated. Four successive 400-ml. portions of the solution were added and evaporated. The final 400-ml. portion was not evaporated. At this stage, the autoclave contained approximately 250 grams of purified lithium hydroxide, some in solution and some in crystal form, and 500 grams of water.

Solubility Determinations. Sampling of the supernatant liquid at temperature was accomplished by opening the sampling valve and allowing the vapor pressure of the system to force the liquid through the filters into the sample receiver. The receivers were 300-ml. Erlenmeyer flasks fitted with two-hole rubber stoppers. A stainless steel tube, with a pressure fitting for attaching to the sampling valve, was inserted through one hole in the stopper. This tube extended nearly to the bottom of the flask. The assembled receiver (consisting of flask, stopper, tube, and about 150 ml. of distilled water) was weighed prior to attachment to the sampling valve. About 5 to 7 grams of the supernatant liquid was slowly taken into the cold water in the flask. The receiver was then reweighed and the weight of the sample obtained by difference. The inside of the tube was rinsed into the flask and the total LiOH determined by titrating with standard hydrochloric acid, using a phenolphthalein indicator. Two receivers were used at each sampling, one to receive the purge solution drawn from the line and the other for the sample.

Three different techniques were used to establish equilibrium.

In the first procedure, the solution in contact with the solid LiOH was agitated at temperature for 16 hours before sampling. Samples were taken every 3 hours thereafter, until successive analyses showed that equilibrium had been attained. The temperature was then raised 50° and the procedure repeated.

The second procedure was similar to the first one except that, 1 hour before sampling, 10 grams of water vapor was allowed to escape from the head space above the solution. This effected a concentration of the solution and helped confirm a condition of equilibrium.

In the third procedure, the solution was sampled as the temperature was decreased in 50° intervals from 650° F. Thus, further confirmation of equilibrium conditions could be established.

Since the vapor pressure was too low to force the liquid through the filters at temperatures below 300° F., sampling at these temperatures was accomplished by partially evacuating the sample receiver. The data at 650° F. were obtained without a filter in the sampling line. Temperature and pressure conditions at this point were such that the solution would flash evaporate in the line between the filter and the valve when the valve was opened. The close agreement of the successive samples indicated that any suspended material had settled and only solution came through the valve. Samples could not be obtained at 680° F. with the present experiment arrangements, as the slightest relief of pressure at the valve caused the line to plug.

Vapor-Pressure Determinations. The vapor-pressure determinations were run in a static 1-liter all-nickel autoclave made by Autoclave Engineers.

A temperature-pressure calibration curve for the gage and thermocouple was first determined by using distilled water. The data presented later have been adjusted, using this calibration curve. Control of the heat to the various sections of the autoclave heater was such that a variation of temperature from top to bottom of the autoclave was no greater than ±1 degree. The dead-weight pressure gage could be read with an accuracy of ±1 p.s.i. at the low pressures to ±5 at the high pressures.

The autoclave was filled by a procedure similar to that described for the solubility determinations.

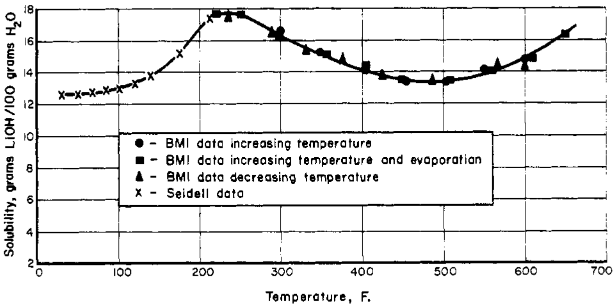


Figure 2. Solubility of lithium hydroxide in water

When vapor-pressure measurements were made on the dilute solutions at increasing temperatures, the solution was withdrawn to maintain a minimum head space in the autoclave as expansion occurred. In the determinations using saturated solutions, some of the water vapor was allowed to escape to maintain the head space required. The volume of the head space was not controlled during the determination with decreasing temperatures.

EXPERIMENTAL RESULTS

Solubility Data. Solubility data are presented in Figure 2. The average values are plotted and show the close agreement obtained by the three techniques. Values from Seidell (*4*) for temperature below 220° F. are included in the plotted data.

The results are interesting in several respects. First, the solubility curve shows a maximum value at about 240° F. and a minimum at about 480° F. and at room temperature. A plot of mole fraction of lithium hydroxide content of saturated solution against temperature shows a more abrupt break in the solubility curve than is evident in Figure 2. A sudden drop in solubility occurs near 250° F. and a rapid increase near 500° F. It is likely that the first break in the curve is related to the phase change from the monohydrate to the anhydrous salt. Other salts (such as lithium carbonate, sodium sulfate, and calcium sulfate) also exhibit inverse solubility as a function of temperature.

The cause for the rise in solubility at 500° F. is less easily explained.

The data also show that increasing the temperature as high as 650° F. did not greatly affect the over-all solubility of lithium hydroxide. For example, values range from a minimum of about 12.7 grams of LiOH per 100 grams of H_2O at room temperature to a maximum of only about 17.7 grams at 240° F.

In contrast to these results, the solubility values of sodium hydroxide show a rapid and fairly uniform increase as temperatures are raised. Values from the *International Critical Tables* (*1*) and from Seidell are presented in Table I for comparison with those for lithium hydroxide obtained in the present study. At 140° F., the solubility of sodium hydroxide is about 20 times that for lithium hydroxide; at 375° F., it is amost 35 times greater; at 563° F., it is about 200 times greater.

Vapor-Pressure Data. The vapor pressures, measured for a saturated lithium hydroxide solution and for solutions containing 5 and 9.4 grams of LiOH per 100 grams of H_2O, are presented in Table II. The values for the depression of the vapor pressure of water (Δp) as affected by the

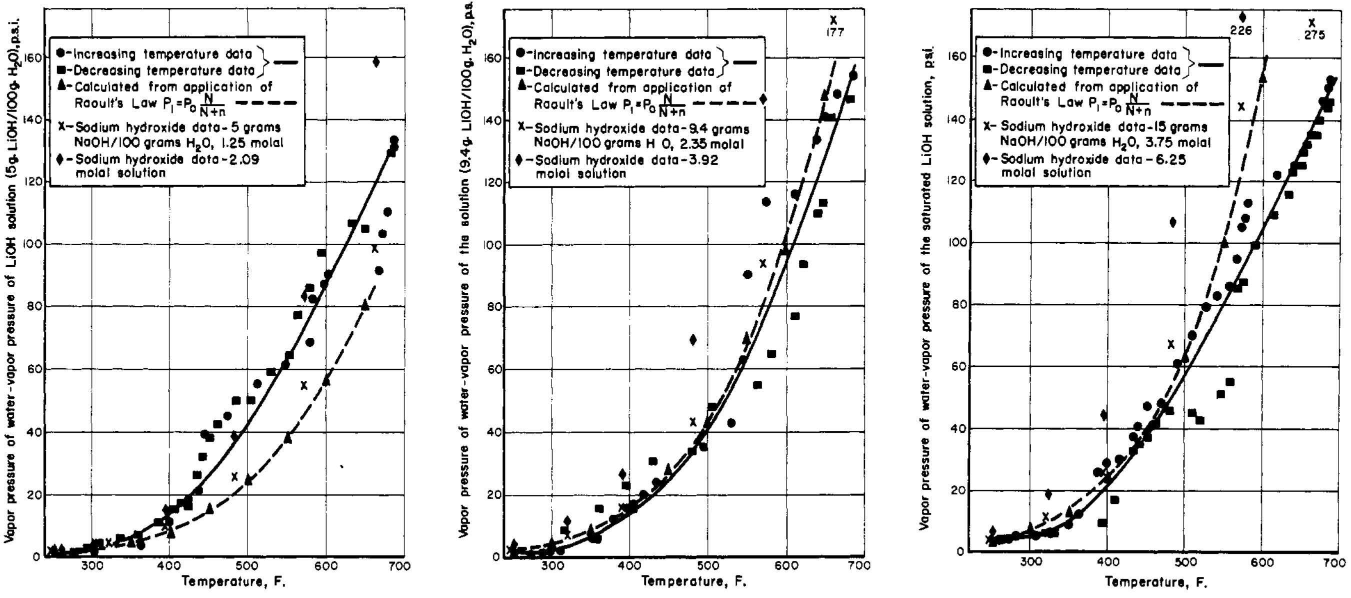
Table I. Solubility of Hydroxides in Water at Elevated Temperatures[a]

	Soly., G./100 G. H_2O	
Temp., ° F.	LiOH	NaOH
140	13.8	292
176	15.3	314
194	16.5	. . .
212	17.5	328
248	17.7	364
284	16.8	392
302	16.6	. . .
320	16.0	424
356	15.2	464
374	14.7	496
402	14.2	600
509	13.5	1067
563	14.1	2930
611	15.0	Melting point

[a] Present study, *1* and *4*.

Table II. Vapor Pressure of Lithium Hydroxide Solutions

Temp., ° F.	*A* Vapor Press. H_2O (Steam-Table Data), P.S.I.A.	*B* Vapor Press. Soln., P.S.I.A.	Vapor-Press. Depression ($A - B = \Delta p$), P.S.I.
5 G. LiOH per 100 G. H_2O (2.09 molal)			
Ascending:			
238	24	23	1
303	70	69	1
363	159	156	3
399.5	245	234	11
424	322	304	18
438	373	352	21
446	405	366	39
474	534	489	45
513	765	710	55
548	1028	967	61
580	1327	1259	68
584	1368	1286	82
599	1538	1451	87
604	1710	1620	90
669	2515	2424	91
672.5	2574	2469	103
680.5	2714	2604	110
687.5	2840	2709	131
Descending:			
683	2763	2634	129
650.5	2215	2109	104
631	1940	1834	106
593	1465	1368	97
579	1310	1224	86
563	1161	1084	77
550.5	1048	984	64
529	878	819	59
504	706	656	50
484	588	538	50
473	529	484	45
461	471	429	42
450	423	385	38
441	386	354	32
433	355	329	26
423	319	303	16
413	286	269	17
407	267	252	15
384	205	194	11
359	151	144	7
334	108	102	6
307	74	70	4
293	60	58	2
277	47	46	1
237	22.5	22	0.5
9.4 G. LiOH per 100 G. H_2O (3.92 molal)			
Ascending:			
275	45	44	1
289	56.5	55	1.5
298	65	63	2
312	80	78	2
354	141	135	6
360	153	147	6
379	193	181	12
395	233	217	16
406	265	248	17
418	303	283	20
435	364	340	24
497	663	628	35
531	892	849	43
547	1020	957	63
511	1054	964	90
595	1487	1374	113
613	1705	1589	116
644	2128	2094	134
654.5	2280	2139	141
667	2478	2330	148
689	2876	2722	154
Descending:			
684	2763	2616	147
658	2330	2289	141
649	2193	2079	114
644.5	2133	2028	105
9.4 G. LiOH per 100 G. H_2O (3.92 molal)			
Descending:			
623	1826	1732	94
612	1686	1609	77
572	1247	1185	62
566	1189	1134	55
506.5	722	674	48
480.5	568	534	34
430	343	312	31
396	237	214	23
362	157	141	16
316	85	76	9
251	30	28	2
Saturated Lithium Hydroxide			
Ascending:			
261	36	32	4
263	37	33	4
273.5	45	41	4
282	51	46	5
307.5	75	70	5
328	100	94	6
349	133	124	9
363	158	146	12
387	213	187	26
398	241	212	29
415	281	251	30
433	355	318	37
438	374	334	40
456	431	384	47
470	515	462	48
490	622	561	61
511	752	682	70
528	870	791	79
543	987	904	83
558	1115	1029	86
566	1189	1094	95
574	1266	1161	105
578	1307	1199	108
581	1337	1224	113
620	1786	1664	122
641	2074	1949	125
678.5	2680	2534	146
682	2745	2594	151
685	2800	2649	151
688	2857	2699	158
Descending:			
684.5	2790	2644	146
683	2763	2619	144
676	2636	2496	140
671	2549	2414	135
666	2464	2329	135
658	2323	2201	132
653.5	2265	2136	129
652	2239	2114	125
639	2045	1922	123
635	1988	1872	116
613	1698	1589	109
588	1511	1312	99
575	1276	1189	87
566.5	1185	1099	86
559	1124	1064	60
547	1020	964	56
518.5	782	734	48
510	744	694	50
480.5	568	522	46
464	486	444	42
452.5	433	396	37
442	389	354	35
433	355	322	33
408	271	254	17
391	223	214	9
333	107	101	6
320.5	90	84	6
275	45	41	4



Figures 3, 4, and 5. Depression of vapor pressure

addition of lithium hydroxide are also presented in the table and graphically illustrated in Figures 3, 4, and 5. Included in the curves are calculated values for Δp obtained by Raoult's law, $P_1 = P_0(N/N + n)$. Values for sodium hydroxide, as taken from the International Critical Tables (*1*), are presented for the same molalities and weight per cent concentrations as those used for lithium hydroxide. Values were obtained on an ascending temperature schedule and also on a descending schedule.

Table II shows that the vapor depression of the 2.09-molal lithium hydroxide solution amounts to about 130 p.s.i. at about 685° F. In Figure 3, these Δp values are compared with those for sodium hydroxide.

Lithium hydroxide causes somewhat more depression than does sodium hydroxide at equal concentrations by weight. At equal molalities, however, sodium hydroxide causes more lowering of pressure.

The distortion in the Δp curve (Figure 3) near 480° F. occurs at the same temperature as the minimum in the solubility curve (Figure 2). The cause of this effect is not understood and the occurrence may be entirely coincidental.

Figure 3 shows that the deviation from Raoult's law is positive and appreciable for 2.09-molal lithium hydroxide solutions. On the other hand, it is negative for the more concentrated solutions. These data are strengthened by the report from the Bettis Laboratory (*3*) on the basis of conductivity measurements that the ionization of LiOH decreases as the temperature is raised. An equally valid explanation is that variation in association phenomena causes the effect noted.

Table II and Figures 4 and 5 show that the vapor depression for a 3.92-molal solution and for a saturated solution (about 6.25 molal) of lithium hydroxide amounts to about 154 and 158 p.s.i., respectively, at about 689° F. In general, over the entire temperature range studied, the saturated solution showed slightly greater vapor-depression values than did the 3.92-molal solution.

These colligative properties of lithium hydroxide solutions are dependent on the activities of the species as well as on the degree of dissociation and association. Thus, the positive and negative deviations from Raoult's law noted for the various solutions can probably be explained. The data are not sufficiently precise to furnish a more complete interpretation.

The Δp values for sodium hydroxide are much higher than those for the lithium hydroxide solutions. Table III summarizes the values for lithium and sodium hydroxide at three concentrations expressed as molality, grams per

Table III. Vapor-Pressure-Depression Data for Lithium and Sodium Hydroxide Solutions of Equivalent Concentrations[a]

Concentration	LiOH	NaOH		LiOH	NaOH		LiOH	NaOH	
G. per 100 G. H_2O	5	5	8.4	10	10	15.6	15[b]	15	25
Weight per cent	4.76	4.76	7.83	8.59	8.59	13.5	13.04	13.04	20.0
Molality	2.09	1.25	2.09	3.92	2.35	3.92	6.25	3.75	6.25
Vapor-pressure depression (Δp), p.s.i.									
248° F.	1	1.2	1.95	1	2.25	4	4	3.6	6.7
320° F.	4.5	3.6	6.3	3	7.15	11.5	7	11.2	18.8
392° F.	12.5	9	14.5	13	16	27	18	26	44
482° F.	35.5	25	38	34	42.5	69	50	67	107
572° F.	73	52	83	74	93	147	90	144	226
662° F.	120	98	158	140	177	280	137	275	433

[a] NaOH data calculated from vapor-pressure data in *International Critical Tables*; LiOH data calculated from smooth curves in,Figures 3, 4, and 5 of this report. [b] Saturated, approximately.

100 grams H_2O, and weight per cent. At 662° F., the vapor depression for a 6.25-molal sodium hydroxide solution is about three times as great as for a lithium hydroxide solution of the same molal strength. More dilute solutions showed smaller differences. In other words, sodium hydroxide shows a greater lowering of vapor pressure than does lithium hydroxide at the same molal concentrations. In addition, the extent of this difference increases as the concentration of the solution rises. Data for sodium hydroxide, as given in the *International Critical Tables* (*1*), have been confirmed recently by Kiyama and Kitahara (*2*).

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Vapor Pressure of Glycerol

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RECENT INTEREST in the properties of highly polar compounds (*1, 5, 10*) has indicated the lack of reliable information concerning the vapor pressure of glycerol in the range from room temperature to about 100° C. The accepted high temperature values were obtained by Stedman (*9*) from an extrapolation of data on the equilibrium concentrations of glycerol in water solutions at known temperatures and pressures. He plotted partial pressure of glycerol against total pressure and extrapolated to the point where the two were equal. At 70° C., however, only two points were available; at 60° and again at 50° only one point is given. The latter two were at very low glycerol concentration and thus the vapor pressures reported represent only an estimate of the proper values.

Low temperature data available are the single effusion value obtained by Wyllie (*11*) at 18° C. for glycerol of unknown purity and the effusion results obtained by Zil'berman-Granovskaya (*12*), after repeated distillations and thus possibly subject to thermal decomposition. The heat of vaporization calculated from this latter study was only 4.9 kcal./gram-mole, less than one third of the value expected for such a highly polar substance (*1*). Filosofo and co-workers (*4*) measured the pressure of glycerol atmospheres with a fiber vacuum gage at three temperatures below 50° C. and obtained values in reasonable agreement with the extrapolation of Stedman's data.

EXPERIMENTAL

Method Selected. Because of the extremely low volatility of glycerol at room temperature, Knudsen's vapor effusion technique (*6*) was chosen for vapor pressure determination. The Knudsen equation relates the rate of efflux of a vapor through an orifice to the pressure differential, provided the major dimension of the opening is much less than the mean free path of a molecule in the gas phase.

$$-\frac{1\,\mathrm{d}W}{A_o\mathrm{d}\theta} = \left(\frac{M}{2\pi RT}\right)^{1/2}\left(P_v' - P\right) \qquad (1)$$

Clausing (*3*) has calculated the probability that molecules entering a cylindrical canal in free molecule flow will reach the exit without being reflected back through the entrance. Such efficiency factors may be evaluated both for the orifice itself and for the body of the cell. Ross has shown (*8*) that for a cell with diameter equal to height the cell body correction is negligible, and the cell pressure may be related to the vapor pressure as in Equation 2

$$P_v = (1 + W_bA_o/\alpha A_s)\,P_v' \qquad (2)$$

where α is the evaporation coefficient and the effusion is assumed to be into very high vacuum. A value for α of 0.05 was used in this correction in accord with the most recently reported coefficient for glycerol surfaces (*5*). This calculation (Table I, column 5) is not sensitive to the value of α used.

When the orifice area in Equation 1 is modified by the Clausing factor, these two equations may be combined to yield the final form used to calculate vapor pressures.

$$P_v - P = -\frac{\mathrm{d}W}{\mathrm{d}\theta}\left(\frac{1+\frac{W_bA_o}{\alpha A_s}}{W_bA_o}\right)\left(\frac{2\pi RT}{M}\right)^{1/2} \qquad (3)$$

Apparatus and Procedure. The effusion systems used in this work, similar in design to those of Bradley (*2*), are shown schematically in Figure 1. The basic components of each system were the spring case, quartz spring, effusion cell, liquid nitrogen cold trap, diffusion pump, and mechanical vacuum pump.

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