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Thermal expansion of reference materials: copper, silica and silicon

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Abstract. Between 30 and 290 K the thermal expansion of vitreous silica is shown to be particularly sensitive to thermal history. Values given for the linear coefficient α were determined relative to copper, and existing reference data for copper are discussed. α for silicon has also been measured relative to copper from 55 K to room temperature. Values of α at 283 K are reported for a number of samples of copper, and for Ag, Au, Al, Pt, Pd, MgO, NaCl and CaF_2.

1. Introduction

Whilst investigating the thermal expansion of vitreous silicas and some related low-expansion materials at temperatures below 30 K, we have made additional measurements at intermediate temperatures from 55 to 145 K and 195 to 220 K which confirm that the thermal history (or density) of silica has a profound effect on its expansion characteristics. This effect is much larger near 100 K than it is below 30 K (White and Birch 1965) or at higher temperatures (eg Brückner 1962). Silica is often used as a reference material in dilatometry, so we have sought to establish the absolute values of the linear expansion coefficient as a function of temperature for samples of different 'fictive' temperatures. As the measurements were made in a dilatometer, relative to copper, this has led us to examine carefully the published reference data on copper.

The data on copper above 30 K are principally from Rubin *et al* (1954), Leksina and Novikova (1963), Lifanov and Sherstyukov (1968) and Hahn (1970). These measurements agree well among themselves from about 130 to 220 K but differ significantly below and above this. There are also unpublished data from the National Research Council of Canada (C G Kirby and H Preston-Thomas 1968) which agree closely with the values of Hahn (US NBS) at room temperature and indeed down to 130 K, whereas those of Rubin *et al* and the Russian data are about 1% higher at room temperature. Below 130 K, we use smoothed values based on results of Rubin *et al.* The alternative results of Hahn show scatter below 100 K, do not join smoothly with the low-temperature data (eg White and Collins 1972), and are not corroborated by later NBS measurements (Kirby and Hahn 1970, private communication).

In this paper we also report measurements on silicon made in the copper cell and compare results with earlier absolute values obtained here by Carr *et al* (1965) and with measurements by Ibach (1969). Silicon is a useful reference material, as it is readily available in a high state of purity and has a small and isotropic expansion coefficient arising partly from its diamond structure. It has a high Debye characteristic temperature, so that α is particularly small below 30 K.

Values of α at 283 K (average from 0 to 20 °C) for a number of materials have been recalculated from our earlier measurements by using α (copper) $= 16{\cdot}43 \times 10^{-6}\ \mathrm{K}^{-1}$, ie the NBS–NRC value, and including a small correction ($< 1\%$) arising from expansion of the capacitor plate which had been calculated incorrectly in our earlier reports (eg White and Pawlowicz 1970, White 1972, White and Collins 1972).

2. Measurements

The expansions were measured in a three-terminal capacitance cell (White and Collins 1972) made of OFHC copper. Specimens are 40–50 mm in length and about 15 mm in diameter. Platinum and germanium thermometers are attached to to the dilatometer and have been calibrated here at the National Standard Laboratory. This relative cell and its electronic temperature controller were intended for measurements below about 30 K, but with liquid oxygen in a pumped chamber temperatures of 55 to 90 K are easily accessible. The controller can heat the cell up to about 146 K with liquid oxygen as refrigerant and to about 220 K with solid carbon dioxide (and acetone) as refrigerant.

Specimens include the following vitreous silicas given to us after thermal ageing by Dr G Hetherington of Thermal Syndicate Limited (see White and Birch 1965 for details including densities):

(i) Spectrosil 1000 aged at 1000 °C for hundreds of hours;
(ii) Spectrosil 1400 aged at 1400 °C;
(iii) IR Vitreosil which as received has a fictive temperature of 1050–1150 °C (G Hetherington, private communication);
(iv) Vitreosil 1400 aged at 1400 °C;
(v) Silicon Si1, 100 Ω cm n-type plated with 0·02 mm layer of nickel and evaporated gold (White and Collins 1972).

3. Data for copper

There have been many measurements of the expansion of copper including those listed by Corruccini and Gniewek (1961), by Lifanov and Sherstyukov (1968), and by Hahn (1970). Comparatively few show sufficient stated accuracy or internal consistency to be used as reference data. We have considered above 35 K the values of Rubin *et al* (1954), Leksina and Novikova (1963), Lifanov and Sherstyukov (1968), and Hahn (1970), which all have uncertainties of $\leqslant 1\%$ or $\leqslant 0{\cdot}1 \times 10^{-6}\ \mathrm{K}^{-1}$ in the linear coefficient α.

For purposes of comparison and smoothing, we have calculated values of the Grüneisen or anharmonicity parameter

$$\gamma = \frac{\beta V B_{\mathrm{S}}}{C_p} \equiv \frac{\beta V B_{\mathrm{T}}}{C_v},$$

where $\beta = 3\alpha$ for isotropic solids, V is the atomic volume, C_p and C_v are specific heats at constant pressure and constant volume respectively, and B_{S} and B_{T} are respectively the adiabatic and isothermal bulk moduli. $\gamma(T)$, like the Debye temperature $\theta(T)$, is an average over the lattice spectrum and as such should be a smoothly varying function of T, with limiting values at low temperatures, γ_0, and at high temperatures, γ_∞, which do not differ by more than 10 or 20% for isotropic metals (eg Barron 1955).

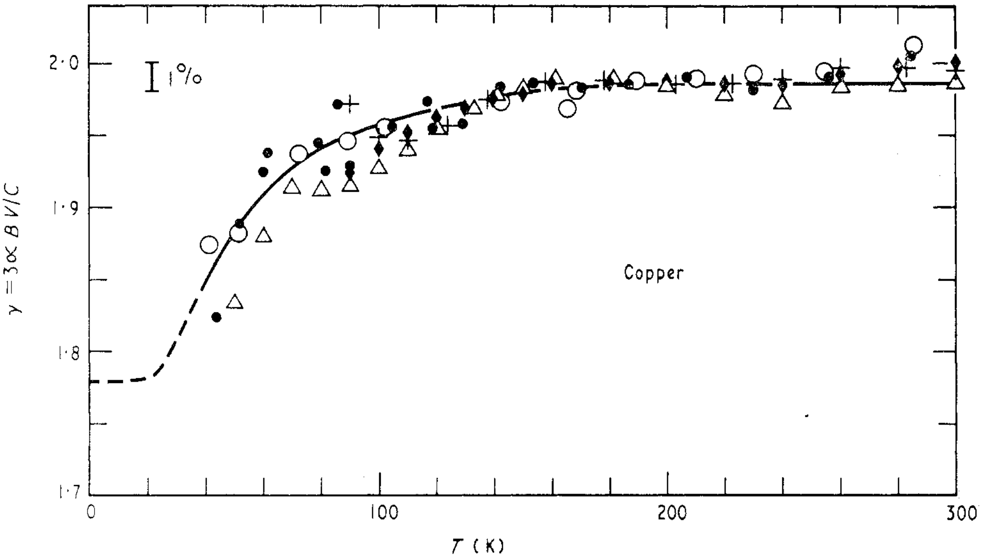

Figure 1. Grüneisen parameter γ for copper: ○ Rubin *et al* 1954 single crystal; ● Rubin *et al* polycrystal; ◆ Leksina and Novikova 1963; + Lifanov and Sherstyukov 1968; △ Hahn 1970; — — — White and Collins 1972; ——— smoothed value.

Table 1. Smoothed data for copper

T (K)	Atomic volume V (ml)	Bulk modulus B_S (Mbar)	Heat capacity C_p (J (g at)$^{-1}$ K^{-1})	γ ($=3\alpha VB_S/C_p$)	Linear coefficient α (10^{-6} K^{-1})
30	7·04	1·420	1·693	1·810	1·01
40	7·04	1·419	3·740	1·850	2·31
50	7·04	1·418	6·154	1·885	3·87
60	7·04	1·417	8·595	1·914	5·50
70	7·04	1·416	10·86	1·928	7·00
80	7·05	1·415	12·85	1·940	8·33
90	7·05	1·413	14·56	1·950	9·50
100	7·05	1·412	16·01	1·958	10·50
110	7·05	1·410	17·22	1·963	11·33
120	7·06	1·408	18·25	1·968	12·04
140	7·06	1·405	19·87	1·977	13·20
160	7·07	1·401	21·05	1·982	14·04
180	7·07	1·397	21·94	1·985	14·70
200	7·08	1·393	22·63	1·985	15·18
220	7·08	1·389	23·17	1·985	15·58
240	7·09	1·384	23·60	1·985	15·91
260	7·10	1·380	23·94	1·985	16·17
280	7·11	1·375	24·22	1·985	16·39
283	7·11	1·374	24·26	1·985	16·43
300	7·11	1·371	24·46	1·986	16·61

The values of γ in figure 1 and table 1 were calculated using values of V from x-ray density and expansivity data; B_S was taken from the elastic moduli of Overton and Gaffney (1955). These might be in error in absolute terms by as much as 1 % but should not introduce significant random errors into our γ values. C_p was taken from the critical compilation by Furukawa *et al* (1968) in which uncertainties do not seem to exceed 0·2%. Hence where differences in γ (figure 1) reach 1% or more (ie outside the range 130 to 230 K) they must arise largely from corresponding differences in α values. The smooth curve in figure 1 has been chosen to join the low-temperature values of γ (lattice) given by White and Collins (1972) below 35 K, values of Rubin *et al* from about 40 to 140 K, and those of Hahn near room temperature. As mentioned in the introduction, we chose the NBS or Hahn values here because they were closely corroborated by data from NRC (C G Kirby and H Preson-Thomas 1968, unpublished: for example, NBS and NRC both give $\alpha(283\ \mathrm{K}) = 16{\cdot}43 \times 10^{-6}\ \mathrm{K}^{-1}$, whereas recent Russian values give $16{\cdot}53 \times 10^{-6}$. The values for other common solids which we have measured (relative to copper) will be discussed below. These suggest that between 250 and 300 K the smooth curve might be better chosen midway between the Russian and NBS data. Below 130 K we prefer the values of Rubin to those of Hahn for reasons mentioned above in the introduction.

Table 2. Some comparative values for measured length changes of copper, $10^6 \Delta l/l$, relative to 293·15 K

T (K)	NBS(a)	NBS(b)	NRC(c)	L&S(d)	R, A&J(e)
25	−3237	−3244	—	—	−3258
50	−3187	−3196	—	—	—3206
100	−2817	−2821	−2810	−2830	−2829
150	−2207	−2205	−2203	−2218	−2217
200	−1480	—	−1482	−1490	−1491
273·15	−326	—	−329	−328	—330
293·15	0	0	0	0	0

(*a*) Values for NBS reference material #736 (Hahn 1970).
(*b*) Private communication from R K Kirby and T A Hahn, NBS, Washington, 1970.
(*c*) Private communication from C G Kirby and H Preston-Thomas, NRC, Ottawa, 1968.
(*d*) Lifanov and Sherstyukov 1968.
(*e*) Rubin *et al* 1954.

Table 2 illustrates differences in integrated length changes reported for copper. These differences of 10–20 ppm in $\Delta l/l$ arise presumably from measurement inaccuracies rather than from differences in the copper samples. Our experience (see White 1972 and table 4) shows that cold working and impurity levels of $<0{\cdot}1$ % do not have measurable effects at temperatures above 30 or 40 K. This experience is consistent with heat capacity measurements which show that cold work and trace impurities do not alter C_p significantly (eg Martin 1960, Furukawa *et al* 1968) at temperatures where lattice vibrational energy is dominant. Only at lower temperatures do magnetic impurities change the characteristics markedly.

4. Results for silica

Our experimental values of α for different silica specimens are shown in figure 2 and table 3, together with data from Beattie *et al* (1941), Gibbons (1959) and Hahn and Kirby (1972) for standard reference material #739. Differences in fictive temperatures or annealing history are more important than the type of silica; note that Spectrosil is synthetic silica and Vitreosil is electrically fused from quartz powder.

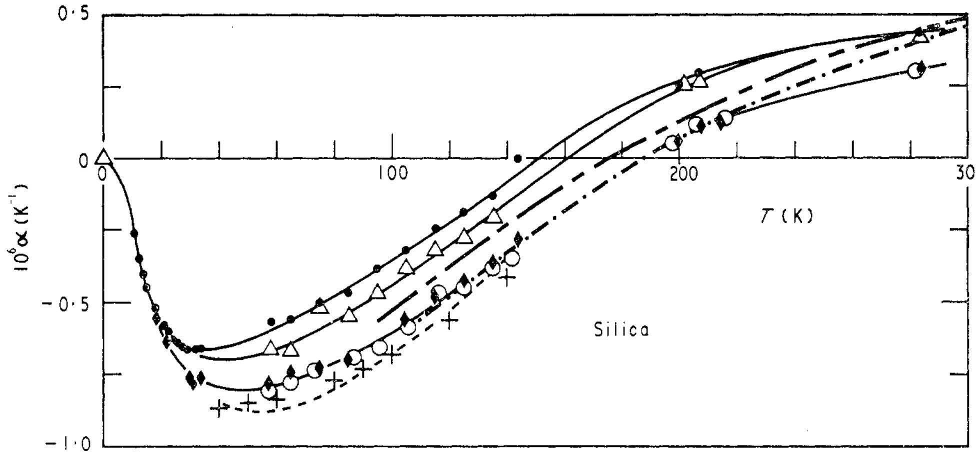

Figure 2. Linear coefficient of thermal expansion α for vitreous silica: —●— Spectrosil 1000; —△— I R Vitreosil; - -○- - Spectrosil 1400; ◆ Vitreosil 1400; - - - Spectrosil and Vitreosil 1400 using α(Cu) from Hahn; — — — SRM 739, Hahn and Kirby 1972; —·— Beattie *et al* 1941; + Gibbons 1959.

Table 3. Linear coefficients for silica and silicon in units of $10^{-6}\,K^{-1}$. (Values above 50 K are based on smoothed values of α for copper discussed in text; values at 40 K are interpolated.)

T (K)	Spectrosil 1000	IR Vitreosil 1100	Spectrosil 1400	Vitreosil 1400	Silicon Sil
10	−0·23	—	—	−0·22	—
20	−0·56	—	—	−0·60	0·00
30	−0·67	—	—	−0·77	−0·05
40	−0·65	−0·70	−0·80	−0·80	−0·15
57·5	−0·58	−0·67	−0·81	−0·78	−0·32
65	−0·56	−0·67	−0·79	−0·74	−0·43
75	−0·50	—	−0·74	−0·73	−0·45
85	−0·47	−0·55	−0·70	−0·70	−0·46
95	−0·38	−0·47	−0·66	—	−0·41
105	−0·32	−0·38	−0·59	−0·56	−0·24
115	−0·24	−0·32	−0·47	−0·48	−0·10
125	−0·19	−0·28	−0·45	−0·43	0
135	−0·13	−0·21	−0·38	−0·36	0·26
143	0·00	—	−0·35	−0·28	—
199	0·26	0·26	0·06	0·06	1·38
207	0·30	0·26	0·12	0·11	1·56
215	0·36	—	0·14	0·12	—
283	0·44	0·42	0·30	0·31	2·35

Our values near 30 K and below depend upon a calibration with silicon rods and are unlikely to be in error by more than $0{\cdot}01\times10^{-6}\,K^{-1}$, but at higher temperatures we use the smoothed values for copper discussed above. If these were in error by being, say, $0{\cdot}1\times10^{-6}\,K^{-1}$ too high below 100 K, then all the silica values would be high by a corresponding amount. The lowest broken line in figure 2 shows the effect of using the NBS reference data for copper (Hahn 1970). Likewise at 283 K where we have used the NBS-NRC value for copper, $16{\cdot}43\times10^{-6}\,K^{-1}$, a choice of 16·48 or $16{\cdot}53\times10^{-6}\,K^{-1}$ would increase the α values for silica by 0·05 or $0{\cdot}10 \times 10^{-6}\,K^{-1}$ respectively, making our values for 1400 °C material agree better with those of Beattie *et al* (1941).

For comparison the SRM 739 in figure 2 was fused silica aged at 1100 °C for 7 h. The silica measured by Beattie is stated to have been flame worked and therefore to have 'characteristics of a high fictive temperature' (see Hahn and Kirby 1972). We are not aware of the thermal history of the silica used by Gibbons (1959). The integrated net changes in length per unit length between liquid helium temperature and 293 K from our data are:

1000 °C silica	-16×10^{-6}
~1100 °C silica	-29×10^{-6}
1400 °C silica	-70×10^{-6}.

Changes resulting from choice of other copper reference data could increase the *magnitude* of each of these by $5\text{–}9 \times 10^{-6}$.

The expansion behaviour of vitreous silica at low temperatures, particularly at liquid helium temperatures, is of some basic interest and will be presented in more detail elsewhere, together with data on some other low-expansion materials.

5. Results for silicon

Table 3 and figure 3 give values for silicon obtained in our relative cell and corrected for copper using the smoothed data discussed above. For comparison absolute values are shown from Carr *et al* (1965) and Ibach (1969), which agree with each other below 50 K and for 90–200 K. Between about 60 and 90 K the Ibach values for silicon are up to $0{\cdot}1 \times 10^{-6}\,K^{-1}$ higher (ie less negative) than those of Carr *et al*, and from 250 to 300 K they are about $0{\cdot}1 \times 10^{-6}$ smaller. The present measurements from 60 to 90 K lie between

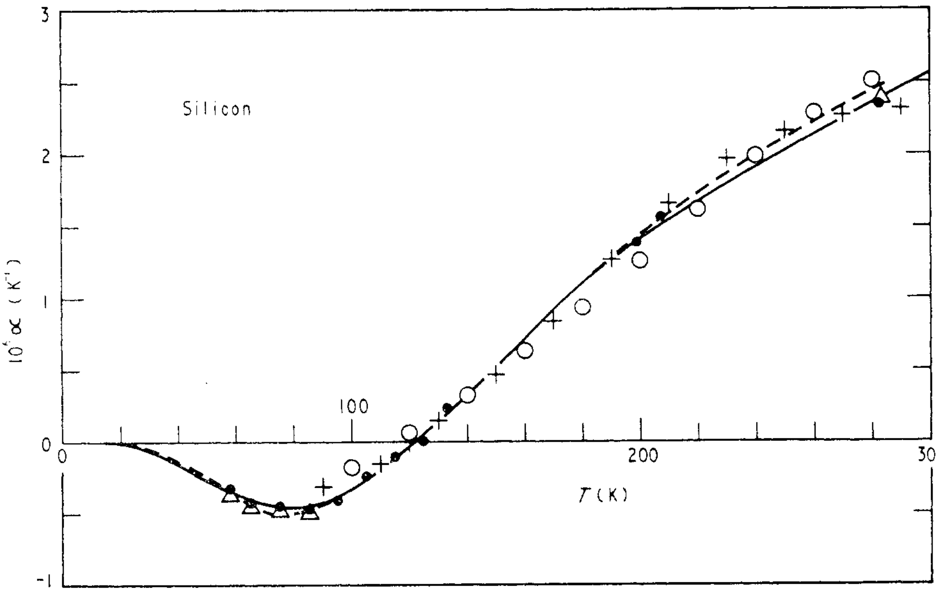

Figure 3. α for silicon: △ Si1 1970 and ● Si1 1973 using 'smoothed' α(Cu); + Gibbons 1958; ○ Batchelder and Simmons 1964; —— Ibach 1969; - - - Carr *et al* 1965.

these and suggest that our choice of copper values cannot be in error by more than about $0{\cdot}05\times10^{-6}\ \mathrm{K}^{-1}$. At 283 K our various measurements between 1970 and 1973 give values of $2{\cdot}34$ to $2{\cdot}37\times10^{-6}\ \mathrm{K}^{-1}$ (using $\alpha=16{\cdot}43\times10^{-6}\ \mathrm{K}^{-1}$ for copper) compared with Ibach's value of $2{\cdot}39\times10^{-6}$ and $2{\cdot}46\times10^{-6}$ from Carr *et al.* This is slight evidence in favour of a larger value of α for copper at room temperature.

6. Values of α at 283 K

Table 4 lists some values of α for coppers, silver, aluminium, magnesium oxide, rare metals, etc, which have been recalculated from our earlier data using $\alpha=16{\cdot}43\times10^{-6}\ \mathrm{K}^{-1}$ for pure copper and a slightly different correction for expansion of the condenser plate in our capacitance gauge. Most of the values are only altered by $0{\cdot}02$–$0{\cdot}04\times10^{-6}$ due to change in this correction. Exceptions are Pd, Ir and Rh for which α is reduced by nearly $0{\cdot}2\times10^{-6}$ compared with our earlier published values which were based on $\alpha=16{\cdot}6\times10^{-6}$ for copper.

Table 4. NSL values of linear coefficient α (units of $10^{-6}\ \mathrm{K}^{-1}$) at 283 K, based on α (copper) $=16{\cdot}43\times10^{-6}$

Material		α	Previous reference
Cu	Asarco	16·43	White 1972
Cu	OFHC	16·43	White 1972
Cu	Dilatometer OFHC	16·43	White 1972
Cu	Electrolytic	16·40	White 1972
Cu	+Te, free machining	16·45	White 1972
Cu	Phosphorus deoxidized	16·46	White 1972
Cu	+0·2% Fe	16·42	White 1972
Cu	+0·2% Mn	16·50	White 1972
Ag	5N	18·76±0·04	White and Collins 1972
Al	6N	22·45	Collins *et al* 1973
Au	5N	14·05±0·04	White and Collins 1972
Ir	>99·9%	6·42	White and Pawlowicz 1970
Pd	3N, 5N	11·60±0·05	White and Pawlowicz 1970
Pt	Engelhard	8·76	White 1972
Rh	>99·9%	8·30±0·10	White and Pawlowicz 1970
MgO	Spicer Crystal	9·84	Unpublished
MgO	Norton Crystal	9·83	White and Anderson 1966
MgO	Irtran 5	9·79	Unpublished
NaCl	NSL	39·10	White and Collins 1973
CaF_2	Harshaw	18·41	Unpublished
ULE 7971	Corning	−0·09	Unpublished
Cer-Vit	Owens-Illinois	−0·07	Unpublished
Zerodur	Schott	−0·20	Unpublished

Except in a few instances, random errors do not appear to exceed $0{\cdot}02\times10^{-6}\ \mathrm{K}^{-1}$.

Values are included for some ultra-low-expansion materials, although their $\alpha(T)$ dependence is more complicated than for silica and probably varies from batch to batch, so they are not likely to be suitable as reference materials. More details and comparison with vitreous silica will be published elsewhere.

7. Discussion and conclusions

The linear expansion coefficient α of a number of copper samples has been measured by Lifanov and Sherstyukov at the VNIIFRI in Moscow and by Kirby and Hahn at the NBS in Washington, who have published averaged reference data for copper. Comparison with earlier values of Rubin *et al*, Leksina and Novikova, etc, shows the following:

(i) Between 130 and 230 K, disagreement is generally $<0{\cdot}2\%$.

(ii) From 230 to 300 K the NBS values are smaller by up to $0{\cdot}1\times10^{-6}$ K^{-1} but are in agreement with unpublished data from the National Research Council of Canada (C G Kirby and H Preston-Thomas).

(iii) The Russian values only extend down to about 100 K where they are somewhat higher than the NBS values. Below 120 K, data from Rubin *et al* are significantly higher (by up to $0{\cdot}1\times10^{-6}$ K^{-1}) than the NBS value, and join more smoothly to the recent low-temperature data of White and Collins (1972) and McLean *et al* (1972).

The data for copper have been smoothed and used to calculate coefficients for different silica samples and silicon which were measured here. The results are generally consistent with other values for silica and silicon, except at 283 K where agreement would be improved by using a value of α for copper larger by about $0{\cdot}05\times10^{-6}$ and therefore closer to the Russian and Rubin values than to those of Kirby and Hahn.

Our conclusion for both copper and silicon is that the linear coefficients given in tables 1, 3 and 4 are known with uncertainties of less than $0{\cdot}1\times10^{-6}$ K^{-1} from 300 K down to liquid helium temperatures, with the corollary that the integrated length change on cooling is known to better than 10×10^{-6} or $0{\cdot}3\%$.

For the individual samples of vitreous silica, coefficients and length changes are given with similar uncertainties, but there are considerable differences between samples with different thermal history. In order to predict the coefficient $\alpha(T)$ to better than $0{\cdot}1\times10^{-6}$ or the integrated change $\Delta l/l$ to better than 10×10^{-6}, the fictive temperature must be well established; for example, 1050 or 1150 °C. Flame-worked silica having $T_f\approx1300$ or 1400 °C will behave very differently from material annealed for a long period at, say, 1100 °C.

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