

State of Arizona  
Bureau of Geology and Mineral Technology

Geological Survey Branch  
Geothermal Group

845 N. Park Ave., Tucson, Arizona 85719  
(602) 626-4391



A MODIFICATION OF THE  
K-Na-Ca CHEMICAL GEOTHERMOMETER  
BASED ON pH VARIATIONS

by

Nile O. Jones  
Sr. Geologist

September 29, 1978

Geothermal Group  
Arizona Bureau of Geology and Mineral Technology  
Tucson, Arizona



## Introduction

The successful application of a K-Na-Ca chemical geothermometer has been fraught with post calculation subjective interpretation. This is due, in part, to deviations from ideality. One line of research deals with pH values. An expression for neutrality over low to moderate temperatures is developed and an additional term added to the empirical expression of Truesdell (1975).

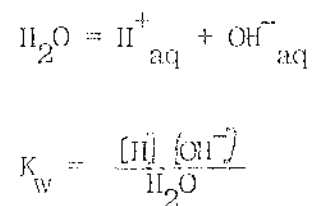
## Discussion

The K-Na-Ca geothermometer of Truesdell (1975) takes the form:

$$t^{\circ}\text{C} = \frac{1647}{\log(\text{Na}/\text{K}) + \beta \log(\text{Ca}^{1/2}/\text{Na}) + 2.24} - 273.15$$

where  $\beta$  may be 4/3 or 1/3 depending on the  $\text{Ca}^{1/2}/\text{Na}$  ratio or the calculated temperature. All geothermometer calculations must be tempered with an understanding of: (1) mineralogy of the immediate system; (2) water chemistry, especially in terms of solubility and chemical equilibrium, and (3) the physical constraints that are placed on the system. We know, for example, that it is improper to apply the K-Na-Ca geothermometer to acidic waters because these elements would probably be out of equilibrium with the common rock-forming feldspar minerals. The question of when this geothermometer can be used must be addressed in view of the low to moderate temperature range and under non-neutral pH conditions.

The equilibrium constant  $K_w$  for the ionization of water is established as follows:



Temperature dependency of  $K_w$  is shown in Table I and Figure 1. A best fit linear equation for temperatures above 30°C is approximately:

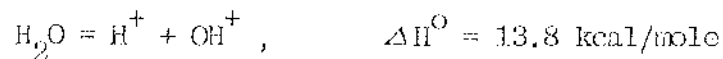
$$\ln K_w(^{\circ}\text{K}) = 0.1178K_w + 4.044$$



This approximation would establish the  $H^+$  and  $OH^-$  activity of pure water at various elevated temperatures. As a first approximation, the neutral pH can be set by dividing the appropriate  $K_w$  by two. Thus the degree of alkalinity or acidity of warm-water springs or wells can be better evaluated.

Numerous other considerations should also be included in the assessment of the activity of an aqueous solution. For example, the activity is lowered by the addition of small quantities of dissolved solutes. Such adjustments would necessitate a reevaluation of the temperature- $K_w$  equation.

Another approach to the problem of equilibrium evaluation may be taken from a thermodynamic point of view. For the reaction:



where  $\Delta H$  is the standard heat (enthalpy) of reaction. The quantitative expression of the effect of temperature upon the equilibrium constant of such a reaction is given as:

$$K_w = Ae^{-\Delta H/RT}$$

Adjustments for activity coefficients, ionic strength, etc. could also be incorporated into the overall consideration of non-neutral pH conditions.

Keeping in mind the mineralogical parameters that constitute the basis for chemical geothermometer calculations, the three most common pitfalls associated with K-Na-Ca temperatures are: (1) high  $CO_2$  concentrations in dilute, high-temperature waters, (2) acid waters in which the common rock-forming minerals have not achieved equilibrium, and (3) mixing of ground water with geothermal water.

One possible modification of the K-Na-Ca empirical geothermometer expression comes about by evaluating the disequilibrium due to the deviation from neutrality. A pH correction can be added to the K-Na-Ca expression such that:

$$t^{\circ}C = \frac{1617}{\log (Na/K) + (Ca^2/Na) \pm \log \left| pH_{obs} - pH_{calc} \right| + 2.23} - 273.15$$



Table 1. Variations of  $K_w$  with temperature.

| $T^{\circ}\text{C}$ | $K_w \times 10^{14}$ | $\log K_w$ |
|---------------------|----------------------|------------|
| 0                   | 0.1139               | 13.056     |
| 5                   | 0.1846               | 13.266     |
| 10                  | 0.2920               | 13.465     |
| 15                  | 0.4505               | 13.651     |
| 20                  | 0.6809               | 13.833     |
| 25                  | 1.008                | 14.003     |
| 30                  | 1.469                | 14.167     |
| 35                  | 2.089                | 14.320     |
| 40                  | 2.919                | 14.465     |
| 45                  | 4.018                | 14.604     |
| 50                  | 5.474                | 14.738     |
| 55                  | 7.297                | 14.863     |
| 60                  | 9.614                | 14.983     |

From: H.S. Horned and B.B. Owen (1958), p. 638.

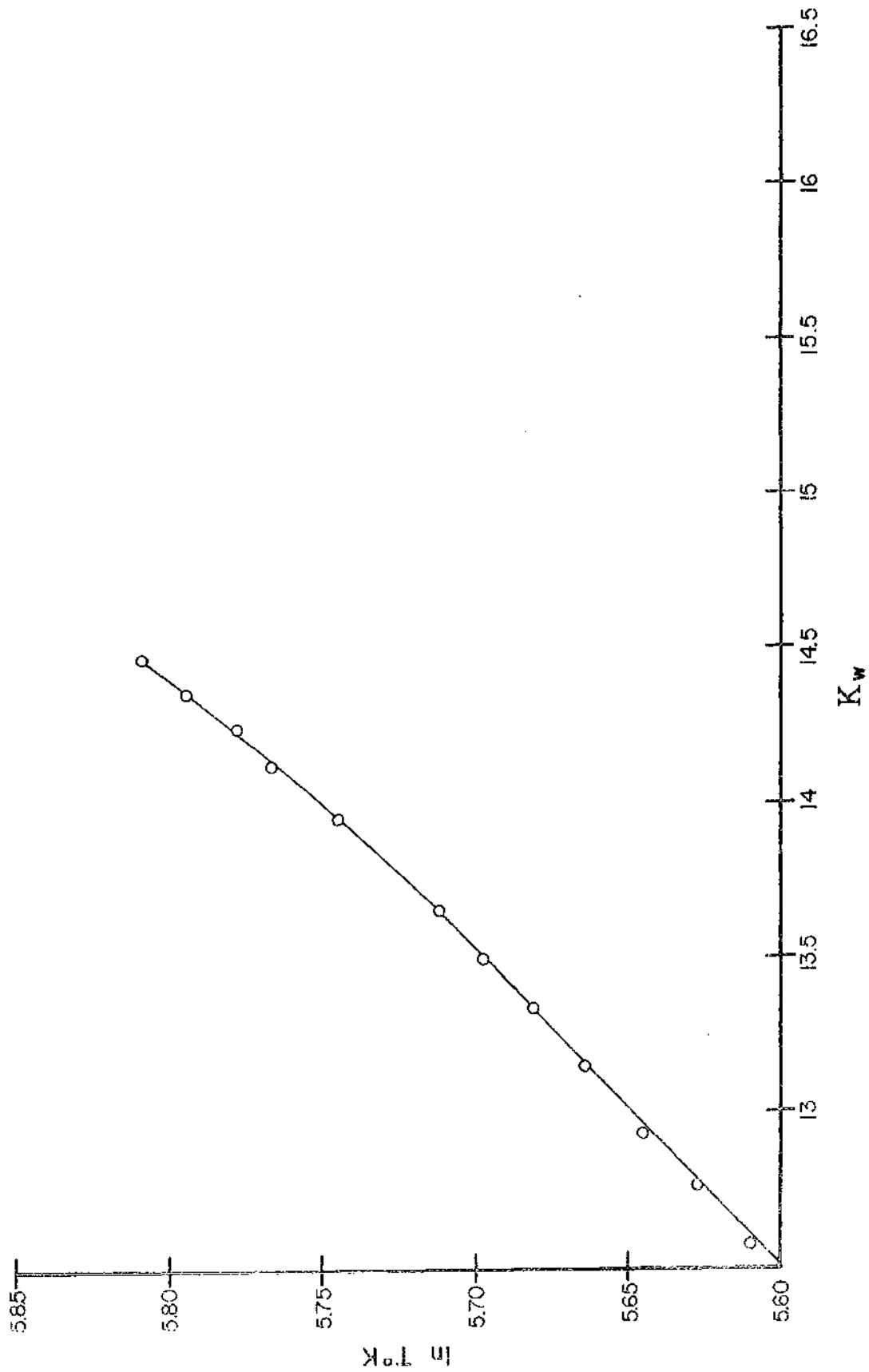


FIGURE 1 -  $K_w$  vs.  $\ln T^{\circ}K$



TABLE 2 Temperature values from various chemical geothermometers

| Data Source | T <sup>OC</sup><br>obs | pH<br>obs | pH<br>calc | Molality x 10 <sup>-6</sup> |       |       | T<br>SiO <sub>2</sub> | T<br>Na-K-Ca | T<br>pH corr. |
|-------------|------------------------|-----------|------------|-----------------------------|-------|-------|-----------------------|--------------|---------------|
|             |                        |           |            | Na                          | K     | Ca    |                       |              |               |
| a           | 49                     | 9.2       | 7.3        | 5.48                        | 0.04  | 0.02  | 120.8                 | 81.2         | 122.9         |
| a           | 67                     | 6.8       | 7.6        | 21.75                       | 1.15  | 1.10  | 148.0                 | 130.7        | 140.6         |
| a           | 40                     | 6.8       | 7.2        | 21.75                       | 0.77  | 0.45  | 159.1                 | 120.2        | 161.4         |
| a           | 77                     | 6.3       | 7.7        | 21.75                       | 0.82  | 0.75  | 159.1                 | 153.1        | 169.9         |
| b           | 43                     | 7.2       | 7.3        | 0.435                       | 0.143 | 0.998 | 81.                   | 220.         | 66.9          |
| b           | 72                     | 6.5       | 7.6        | 1.914                       | 0.358 | 1.397 | 116.                  | 212.         | 144.9         |
| b           | 54                     | 6.6       | 7.4        | 10.004                      | 1.483 | 1.322 | 115.                  | 233.         | 54. *         |
| b           | 72                     | 6.5       | 7.6        | 8.699                       | 0.921 | 1.073 | 123.                  | 210.         | 144.0         |
| b           | 45                     | 6.6       | 7.3        | 2.044                       | 0.332 | 1.297 | 91.                   | 205.         | 128.6         |

\* high sodium relative to calcium; suspected mixed waters

a. Ezio Tongiorgi (ed.), (1970), p. 987-999, 1380.

b. R.H. Mariner, J.B. Rapp, L.M. Willey, and T.S. Presser, (1974), p. 11-19.