tern of their own, which never changed in detail. Flat-fishes control the mottling of their skins through their nervous system; apparently this type of control is entirely absent from the tree toad. The total pattern of the toad becomes sharper or fainter but without local modification of its detail. In the tree toad not the least evidence of differential mottling could be discovered. When these animals were injected with very weak adrenalin they became extremely light and remained so for some hours. On injecting them with pituitrin they became dark and remained so for some time. These two drugs call forth the total natural range of the animal. Such results suggest the conclusion that the tree toad suffers a change of color through internal secretions and not by direct nervous action as in the flat-fishes. Notwithstanding the success with which the tree toad imitates its surroundings, its capacity in this respect must be much more limited than that of the flat-fish and involves merely a lightening or a darkening of its total pattern without local changes in the details.

This conclusion supports the general view advanced by Hogben to the effect that the color changes in amphibians are brought about by humoral rather than by nervous control.

EQUILIBRIUM CONSTANTS OF REACTIONS INVOLVING HYDROXYL: A CORRECTION

By Donald Statler Villars

School of Chemistry, University of Minnesota

In a communication of the above title,[1] two mistakes have come to light which the author wishes to correct in this note.

The first is an arithmetical error in the formula, top of p. 708, for the entropy of oxygen. It should read

$$S_{O_2} = 13.70 + 11.52 \log T - 4.61 \log (1 - e^{-2243.6/T}) + 5R/2 - 4.61 \log P_{atm+} E_{O_2}/T. \tag{1}$$

The wrong formula led to a false value for the entropy of oxygen at 298°K. The corrected value, $S_{O_2 - 298} = 49.2$ cal. degrees^{-1}, is in approximate agreement with the more accurate value of Giauque and Johnston,[2] namely, 49.03, and hence the expectation of a fourth allotropic form of solid oxygen is uncalled for.

The second error is more fundamental and was due to the neglect of the nuclear degeneracy of the hydrogen atom in hydroxyl. It was originally thought by the author that this was automatically taken care of when

one includes all of the rotational terms in the formula for rotational entropy. This is not true, however, and the formula for the entropy of hydroxyl[3] should read

$$S_{OH} = 7.15 + 11.52 \log T - 4.61 \log (1 - e^{-5112/T})$$
$$+ 4.61 \log (4 + 2e^{-197.5/T}) + 5R/2 - 4.61 \log P_{atm} + E_{OH}/T. \quad (2)$$

In order for the free energy calculations to be consistent, therefore, one must add an entropy of $R \ln 2$ for each gram molecule of hydroxyl taking part in those reactions which involve theoretical entropies of hydrogen. Thus, the common logarithms of the equilibrium constants of reactions (1), (3) and (4) of the article cited must be corrected by the corresponding amounts 2 log 2 or 0.6. That no error is introduced by the use of the free energy equations involving calorimetric data is due to the fact that the same correction for nuclear entropy must be added to both sides of the equation, with the result that they cancel out in the difference. This is in agreement with the ideas of Gibson and Heitler,[4] Giauque and Johnston[5] and Rodebush.[6] The corrected equilibrium constants are given in the following table:

EQUILIBRIUM CONSTANTS

TEMP.	LOG K_{O_2} L & R, P. 485	LOG K_{O_2} B & R, P. 96	LOG K_{OH_B}	LOG K_{OH} B & R, P. 96	LOG K_{OH_V}	LOG K_{1B}	LOG K_{1V}	LOG K_{B_4}	LOG K_{4V}
1000	−19.8	−20.1	−21.0	−21.1	−14.7	+1.12	−5.18	+1.91	−4.38
1300	−13.9	−14.01	−14.3	−14.3	− 9.5	+0.43	−4.41	−0.58	−5.42
1500	−11.2	−11.42	−11.3	−11.4	− 7.15	+0.13	−4.06	−1.69	−5.88
1705	− 9.13	− 9.28	− 9.04	− 9.0	− 5.35	−0.10	−3.78	−2.57	−6.26
1900	− 7.55	− 7.6	− 7.28	− 7.2	− 3.97	−0.28	−3.59	−3.22	−6.53
		Interp.							
2155	− 5.94	− 6.08	− 5.47	− 5.5	− 2.55	−0.47	−3.38	−3.94	−6.86
2505	− 4.27	− 4.31	− 3.63	− 3.5	− 1.12	−0.56	−3.15	−4.63	−7.14

$2OH \longrightarrow H_2 + O_2 + 14{,}000$ cal. (B)
$2OH \longrightarrow H_2 + O_2 - 15{,}000$ cal. (V)

---

[1] These PROCEEDINGS, **15**, 705–709 (1929).

[2] Giauque and Johnston, *J. Am. Chem. Soc.*, **51**, 2300–2321 (1929).

[3] The correct calculated value for the entropy of hydroxyl at 298°K. is 45.9 cal. degrees^{-1} mole^{-1}. Owing to our inability to measure calorimetrically the nuclear entropy, the experimentally observed entropy should be less than this amount by 1.4 E. U.

[4] Gibson and Heitler, *Z. Physik*, **49**, 465 (1928).

[5] Private communication. The author wishes to thank Prof. Johnston for his friendly coöperation in locating the arithmetical error which was the cause of the lack of agreement between the two calculated values of the entropy of oxygen and for his communications in which he emphasized the necessity of including the nuclear entropies of the other hydrogen compounds involved in the reactions which were considered. *Cf.* also Giauque, *J. Am. Chem. Soc.*, **51**, 1150 (1929) and *Ind. Eng. Chem.*, **21**, 353 (1929).

[6] Rodebush, *Phys. Rev.*, **35**, 210 (1930).