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Richland, Washington
March 23, 1950

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FROM: W. C. Roesch

P-10 CHEMICAL EQUILIBRIA

There is interest in this system because, though the product of P-10 is T_2 , the chief hazard is considered to be the tritium oxides, and tritium in water vapor might exchange with the hydrogen in the water. At the accepted tolerance concentration of T_2 most of the tritium will exchange if there is a suitable catalyst present. This can be understood rather easily: a T_2 molecule will have a great many more chances to exchange than HTO or T_2O will have to revert to ordinary water, because the number of water molecules will be so much greater than the number of HT or T_2 molecules, which are needed in the latter process. This idea is amplified in the following.

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At 20°C there are 1.7×10^{-5} gm/cc of water vapor in saturated air; this is $a = 9.45 \times 10^{-7}$ moles/cc. At the tolerance for tritium, 10^{-11} curies/cc, there are $b = 1.5 \times 10^{-16}$ moles/cc. Note that $b/a = 1.6 \times 10^{-10}$. As an example, consider the reaction

If K is the equilibrium constant of this reaction and X the number of moles/cc of HTO formed, then

$$K = \frac{X^2}{(a-X)(b-X)}$$

The solution for a and b is

$$X = b \left[1 - \frac{b}{Ka} \right]$$

This indicates that essentially all of the tritium is exchanged; this conclusion will remain true for wide variations in a , b , and K . Accurate knowledge of K is not required; the order of magnitude of K is unity.

It is essential to remember that the conclusion reached here depends upon the presence of a catalyst. If no catalyst is present, it is doubtful if the reaction will proceed at all. The experience with HD has been* that it can be kept in an ordinary vacuum system with water vapor without any measurable exchange taking place; on the other hand charcoal, nickel, etc. will cause the reaction to take place quite rapidly.

Because we do not know what sort of catalyzers may exist at P-10 or in the lungs of a person breathing tritium, a ready answer cannot be given to the question of the importance of these exchange reactions.

The relative amounts of tritium and tritium oxide in the atmosphere at P-10 could be determined by running an air sample through a cold trap and then through a tritium counter (none exists as yet but a possible scheme has been presented). By comparing the counts from the dry air and from the cold trap, the desired ratio could be obtained.

* J. of Chem. Phys. 2, 362 (1934).

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The amount of exchange in the lungs might be estimated by putting a laboratory animal in dried air containing tritium and then later putting it in another cage from which the air could be taken and analyzed as above.

APPENDIX

Another reaction of interest is

It is necessary to give separate consideration to this reaction because there is hydrogen in the atmosphere. Normally, there is 0.01% by volume of hydrogen in the air; this is $c = 4.5 \times 10^{-9}$ moles/cc. Let $b' = 3 \times 10^{-16}$ moles/cc be the concentration of HT and K' be the equilibrium constant. Then

$$K' = \frac{X(c + X)}{(b' - X)(a - X)}$$

The solution for $a \gg c \gg b$ is

$$X = b' \left(1 - \frac{c}{K'a} \right)$$

The same conclusion holds, most of the tritium will be exchanged; however, under wide variations from the conditions of the problem considered, this may not be true. Evidently knowledge of K' is necessary in this case. Fortunately, it is known both experimentally and theoretically*; in the accompanying graph the points are the experimental results and the line gives the semi-theoretical results.

* J. Chem. Phys. 11, 101 and 395 (1943)

Wm. C. Roesch
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