forty-eight hours does not produce any considerable alteration in the composition of human blood or urine.

The investigation is being carried further.

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Equilibria involving calcium, hydrogen, carbonate, bicarbonate, primary, secondary and tertiary phosphate ions.

By I. NEWTON KUGELMASS and A. T. SHOHL.

[*From the Department of Pediatrics, Yale University, New Haven, Conn.*]

The calcium salts of bicarbonate, carbonate, and primary, secondary and tertiary phosphates were studied to ascertain the conditions governing the equilibria at 38°C. Such a system may be evolved theoretically and experimentally by the addition to water of CO_2, $CaCO_3$, Na_2HPO_4. The resulting equilibria may be expressed by the equations

$$CO_2\ (gas) \rightleftarrows CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows H^+ HCO_3^- \rightleftarrows H^+ CO_3^=$$

$$CaCO_3\ (solid) \rightleftarrows CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2 \rightleftarrows Ca^{++} + 2HCO_3^-$$

$$\text{combining } [H^+] + [CaCO_3] \rightleftarrows Ca^{++} + HCO_3^-$$

This resulting equilibria may be expressed according to the mass action law as

$$K_0\,[CO_2] = [H_2CO_3]$$

$$K_1\,[H_2CO_3] = [H^+]\,[HCO_3^-]$$

$$K_2\,[HCO_3^-] = [H^+]\,[CO_3^=]$$

$$K_3 = [Ca^{++}]\,[CO_3^=]$$

$$K_4 = \frac{K_1K_3}{K_2} = \frac{[Ca^{++}]\,[HCO_3^-]^2}{[H_2CO_3]}$$

$$\text{and } K_5 = \frac{K_4}{K_1} = \frac{K_3}{K_2} = \frac{[Ca^{++}]\,[HCO_3^-]}{[H^+]}$$

If we introduce Na_2HPO_4 into such a system

$$HPO_4^{=} + Ca^{++} \rightleftarrows CaHPO_4 \text{ or}$$

$$K_6 = [Ca^{++}][HPO_4^{=}]$$

Multiplying K_5 by K_6 we obtain

$$K_5 \cdot K_6 = \frac{[Ca^{++}]^2 [HCO_3^-][HPO_4^{=}]}{[H^+]} = K_7$$

The complete equilibrium involving $CO_3^=$ and $PO_4^{\equiv}$ takes place when the solution is made more alkaline. This relationship may be derived from the equation

$$HPO_4^{=} \rightleftarrows H^+ + PO_4^{\equiv} \text{ or}$$

$$K_8 = \frac{[H^+][PO_4^{\equiv}]}{[HPO_4^{=}]}$$

Multiplying K_8 by the square of K_7 we obtain

$$K_8(K_7)^2 = \frac{[Ca^{++}]^4 [HCO_3^-]^2 [HPO_4^{=}][PO_4^{\equiv}]}{[H^+]} = K_9$$

Multiplying this by the solubility product constant of $CaCO_3$, K_3, we obtain

$$K_9 \cdot K_3 = \frac{[Ca^{++}]^5 [HCO_3^-]^2 [CO_3^{=}][HPO_4^{=}][PO_4^{\equiv}]}{[H^+]} = K_{10}$$

The above equation for the complete equilibria is not applicable until better values for the third dissociation constant are available. Therefore, the values may be better derived from the simpler relationship for K_7.

This gives a value for the equilibrium in terms of Ca^{++}, HCO_3^-, $HPO_4^=$, and H^+. This value calculated theoretically from known values of the intermediate constants was found to agree well with the experimentally determined value reported elsewhere.[1] The concentration of the ions could be determined

[1] Kugelmass, I. N., and Shohl, A. T., The determination of the equilibria involving calcium, hydrogen, carbonate, bicarbonate, primray, secondary and tertiary phosphat ions., *J. Biol. Chem.*, to appear.

from analysis of all the salts in the system and the calculated degree of ionization. In systems in which this is not possible, due to the presence of unknown compounds as in blood serum, the CO_2 from bicarbonates and H_2CO_3, the P from inorganic phosphates and the H^+ must be determined. The only unknown is the Ca^{++} which may then be calculated from the equation

$$Ca^{++} = \sqrt{\frac{K.\,[H^+]}{[HCO_3^-]\,[HPO_4^{=}]}}$$

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Cystine metabolism. II.

By C. P. SHERWIN and A. R. ROSE.

[*From the Department of Chemistry, Fordham University, New York City.*]

In our last communication[1] we stressed the data bearing on the equilibrium Cystine ⇄ Cystein and gave a general outline of the program of the investigation of cystine metabolism. The twelve preparations of cystine and cystein therein described have been fed to rabbits and the urines corresponding to them have been analyzed. The analysis of the large mass of data is not yet complete. In this communication we will discuss the fate of cystine and cystein as such and one of the derivatives and compare our results with data of other workers, *e. g.*, Wohlgemuth[2], Lewis and Root[3] and Schmidt and Clark[4]. All the figures have been recast so as to give the increase in sulfur in mg. following the administration of cystine sulfur, as cystine or its derivative.

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1 Shiple, G. J., Rose, A. R., and Sherwin, C. P., PROC. SOC. EXP. BIOL. AND MED, 1923, xx, 360.

2 Wohlgemuth, J. Z., *physiol. Chem.*, 1903, xl, 81.

3 Lewis, H. B., and Root, L. E., *J. Biol. Chem.*, 1922, i, 303.

4 Schmidt, C. L. A., and Clark, G. W., *J. Biol. Chem.*, 1922, liii, 193.