pL-methionine in animals treated with carcinogen is under investigation. It is thought possible that increased utilization of S<sup>35</sup> DL-methionine may be associated with a greater potential for growth or regeneration of tissues, a hypothesis that is being tested in normal and protein-depleted rats.

#### References

- 1. WASE, A. W., and ALLISON, J. B. Proc. Soc. Exptl. Biol.
- WASE, A. W., and ALLISON, J. D. 1960. Soc. Lapper. 2000. Med., 73, 147 (1950).
  ALLISON, J. B., et al. Cancer Research, 10, 266 (1950).
  WASE, A. W., and ALLISON, J. B. Abstr., 119th Meeting Am. Chem. Soc. (April 1951).
  WILSON, R. H., DEEDS, F., and Cox, A. J. Cancer Research, 2000 (1990).
- 1, 595 (1941).
- 5. BIELSCHOWSKY, F., and GREEN, H. N. Nature, 149, 526 (1942).
- 6. WASE, A. W., ALLISON, J. B., and MIGLIARESE, J. F. Fed-eration Proc., 11, 307 (1952).

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# On the Anomaly in the Heat Capacity of Manganous Oxide<sup>1</sup>

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Recent work of Todd and Bonnickson (1) on very pure samples of MnO shows that as the temperature increases in the range from 100° to 122° K the heat capacity of MnO rises from about 7 cal/(mole deg) to a peak of 76.7 and then drops sharply to about 7.5. The total heat absorbed is 246 cal/mole. The average Debye heat capacity is about 7, so that  $7 \times 22 = 154$ cal/mole are absorbed by lattice oscillations. One can estimate the additional heat capacity associated with the disappearance of the spontaneous magnetization to be R(2), so that the heat ascribable to this effect is 44 cal/mole. Thus, there is an amount of heat q = 48cal/mole (nearly 20% of the total) which cannot be accounted for by the usual mechanisms.

MnO is antiferromagnetic with  $\theta = -610^{\circ}$  K and  $T_c\simeq 122^\circ$  K, where  $\theta$  and  $T_c$  are the characteristic temperature of the Curie-Weiss law and the Curie temperature, respectively (3). The fact that  $-\theta/T_c$  is equal to 5 rather than unity, as predicted by the simple theory, has been discussed by means of an extension of the molecular field theory to include the effects of nearest and next-nearest neighbor interactions in more complicated orderings of the elementary moments contained in the magnetic sublattices (4). If  $\gamma_1$  and  $\gamma_2$  are the molecular field coefficients for nearest and next-nearest neighbor interactions, respectively, then the ratio  $-\theta/T_c$  for MnO determines  $\rho = \gamma_2/\gamma_1$ , to be 0.75; this value is compatible with two different orderings known as ordering of the second or third kind, which can occur if  $\rho$  is greater or less than 3/4, respectively. Neutron diffraction experiments have shown the ordering below the Curie temperature to be of the second kind (5).

It has been found (6) that the lattice constants of MnO change in this temperature range, and since  $\gamma_1$ <sup>1</sup> Supported in part by the Office of Naval Research.

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and 
$$\gamma_2$$
 (and thence  $\rho$ ) presumably depend strongly  
upon distance, it is suggested that the anomalous be-  
havior can be further interpreted as a change from  
the second to the third kind of order as the tempera-  
ture is increased. To correspond to the neutron diffrac-  
tion results, we should have  $\rho = (3/4) + \delta$  below the  
Curie temperature, and  $\rho = (3/4) - \varepsilon$  throughout the  
transition region to conform to this suggestion ( $\delta$  and  
 $\varepsilon$  are small positive numbers). The following calcula-  
tions provide some quantitative support for this in-  
terpretation.

If  $T_i$  is the Curie temperature for the *i*th kind of ordering, one finds that

$$T_{2} = C \rho \gamma_{1}, T_{3} = C \gamma_{1} [1 - (1/3) \rho],$$
$$-\theta = 3C \gamma_{1} [1 + (1/3) \rho]$$

and

where C is the Curie constant (4). A reasonable expression for the range  $\Delta T$  of the anomalous behavior is  $T_3 - T_2$ , so that we obtain

$$\Delta T = - (\theta/3) \left(1 - \frac{4}{3}\rho\right) \left(1 + \frac{1}{3}\rho\right)^{-1} \approx (16/9) \ T_c \varepsilon.$$

Using the experimental values of  $\Delta T$  and  $T_c$ , we find the estimated value of  $\varepsilon$  to be 0.1. This corresponds to a 13% change in  $\rho$  which is satisfactorily small considering the nature of the calculation.

The energy which must be supplied to the system when in the *i*th kind of ordering in order to destroy the magnetization is of the order of RTi. Thus, for the heat absorbed during the change of ordering, we can write

$$q = R(T_3 - T_2) = (16/9)RT_c \varepsilon$$

From this we find that q = 43 cal/mole, which agrees quite well with the value of 48 given above.

#### References

- 1. TODD, S. S., and BONNICKSON, K. R. J. Am. Chem. Soc., 73,

- YODJ, S. S., and BONNICKSON, K. R. J. Am. Chem. Soc., 73, 3894 (1951).
  Li, Y. Y. Phys. Rev., 84, 721 (1951).
  BIZETTE, H. Ann. phys., 1, 306 (1946).
  NÉEL, L. Ibid., 3, 137 (1948); ANDERSON, P. W. Phys. Rev., 79, 705 (1950); VAN VLECK, J. H. J. phys. radium, 12, 262 (1951); SMART, J. S. Phys. Rev., 86, 968 (1952).
  SHULL, C. G., STRAUSER, W. A., and WOLLAN, E. O. Phys. Rev. 22, 222 (1951)
- Rev., 83, 333 (1951).
- 6. RUHEMANN, B. Phys. Z. USSR, 7, 590 (1935); TOMBS, N. C., and ROOKSBY, H. P. Nature, 165, 442 (1950).

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# Ammoniated Dentifrices and Hamster Caries: Further Studies on the Effects of Ingestion<sup>1</sup>

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Controversy exists concerning the efficacy of ammoniated dentifrices in dental caries prevention. In

<sup>&</sup>lt;sup>1</sup> Work supported by grants-in-aid from the U. S. Public Health Service and from the Graduate School, University of Minnesota.

vitro and in vivo studies that give evidence of effectiveness (1, 2), and others that do not, have been reported (3, 4). A dentifrice containing dibasic ammonium phosphate (5%) and urea (3%) has been advocated. It was believed that the ammonium ion has a specific inhibitory action on the caries process and that the two aforementioned compounds act synergistically in inhibiting decay.

A previous report (5) has shown a reduction in caries in hamsters that ingested a caries-producing diet containing dibasic ammonium phosphate (1%) and urea (0.6%). However, it was also shown, in a toothbrushing study, that a control dentifrice was just as effective as an ammoniated dentifrice in inhibiting hamster caries (6).

The study reported here was designed to test the individual effectiveness of dibasic ammonium phosphate and urea, and to recheck the value of a combination of these compounds. In addition, dibasic sodium phosphate (having the same buffering capacity against acids as dibasic ammonium phosphate) was fed alone and in combination with urea to test the possible specificity of the ammonium ion. occurring solely through chance is also tabulated. The results again show that male animals undergo a greater caries experience during the experimental procedures. In the female mean scores, dibasic ammonium phosphate (Group B) appears to be the most effective in reducing caries experience; urea (Group C) appears to be ineffective; and the combination (Group D) appears to be effective, thus corroborating results of a previous study (5). A similar pattern is shown in the male mean scores.

The statistical tests appear to be highly significant when testing the difference between certain means of the male grouping. A parallel relationship is also apparent in the female grouping. It appears that the ammonium ion does not play a specific role, since dibasic sodium phosphate may be substituted for dibasic ammonium phosphate and the beneficial cariesreducing effect will still be present. Urea in the concentration used (0.6%) did not seem to be effective in reducing the caries scores in the female animals; however, it appeared to be of some value in reducing the caries scores of the male animals. It should be noted that in neither case was an additive or syner-

$\mathbf{TAE}$	SLE 1	
CARIES SC	ORES (	mm²)

	No. animals	Mean <u>+</u> S D		P values		
	no. animais			A	В	С
	Fem	ales				
A, control	12	$500 \pm 132$				
B, 1% $(NH_4)_2$ HPO <sub>4</sub>	30	$399 \pm 122$	в	.02		
C, 0.6% urea	12	$499 \pm 100$	$\mathbf{C}$	.66	.06	
D, 1% $(NH_4)_2HPO_4 + 0.6\%$ urea	25	$415 \pm 119$	$\mathbf{D}$	.06	.66	.13
	· Ma	les				
A, control	15	$706 \pm 171$	в	.001		
B, $2.03\%^*$ (Na) <sub>2</sub> HPO <sub>4</sub> · 7H <sub>2</sub> O	19	$382 \pm 118$	$\mathbf{C}$	.04	.001	
C. 0.6% urea	18	$581 \pm 160$	D	.001	.16	.001
D, $2.03\%^*$ (Na) <sub>2</sub> HPO <sub>4</sub> · 7H <sub>2</sub> O + 0.6% urea	26	$429 \pm 97$				

\* Equivalent in molar concentration to 1% (NH4)2HPO4. The pH of the diets containing the dibasic compounds was 6.7.

After weaning at 21 days of age, 240 animals were divided into eight equal groups and fed a caries-producing diet,<sup>2</sup> beginning at 30 days of age, for 105 days. A sex difference in caries-susceptibility requires a control group for each sex. In the interests of economy, therefore, four groups were females, and four groups males. Table 1 indicates group distribution and drugs tested. Unfortunately, a salmonella epidemic reduced the number of survivors in most groups.

The carious lesions were outlined on charts, blackened with tempera paint, and scored by an instrument employing a photosensitive plate. The total occlusal area affected was recorded in  $mm^2$  (7). The mean caries scores are listed in Table 1. Statistical tests of the difference between means were done. The probability (P) of such a difference between the means

<sup>2</sup> Whole wheat flour, 30%; whole powdered milk, 30%; constarch, 20%; confectioner's sugar, 15%; alfalfa meal, 4%; sodium chloride, 1%.

gistic effect apparent. It would appear that the inhibitory mechanism of the two dibasic compounds tested might result from their buffering action in maintaining an alkaline pH.

Urea may be of aid in preventing dental caries, and further experiments are being conducted to evaluate its position.

### References

- 1. KESEL, R. G., et al. Am. J. Orthodontics Oral Surg., 33, 80 (1947).
- 2. KERR, D. W., and KESEL, R. G. J. Am. Dental Assoc., 42, 180 (1951).
- BIBBY, B. G., and NEVIN, T. A. J. Dental Research, 30, 503 (1951).
  DAVIES, G. N., and KING, R. M. *Ibid.*, 645.
- 5. CHERNAUSEK, D. S., and MITCHELL, D. F. Science, 112, 273 (1950).
- 6. \_\_\_\_\_, J. Dental Research, **30**, 393 (1951). 7. LISANTI, V. F., et al. Ibid., 513.

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