

Phylogenetically, Darwin considered the mammary glands to have developed in response to an intimate relationship existing between mother and offspring as occurs in the lower mammals. Histologically, they have been regarded as both modified sweat and sebaceous glands. Bresslau<sup>3</sup> regards the increased secretory activity of skin glands on particular spots of the abdomen in the lower mammals as due to the presence of highly vascular gland areas. He considers the gland areas to be phylogenetically older than the Mammalia, since they are found on the ventral surface of some birds—the so-called brooding spots. In the higher mammals the mammary glands from their inception are specialised structures the ducts of which, as previously mentioned, appear to owe their inception to an inducing substance; the occasional absence of this substance may be the cause of the blind teats sometimes found.

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<sup>1</sup> *Arch. Entw. Mech. Org.*, **100**, 599.

<sup>2</sup> *J. Exp. Biol.*, **13**, 86.

<sup>3</sup> "The Mammary Apparatus of the Mammalia" (Methuen).

#### Dissociation Energies of CO and CN, and Heat of Sublimation of Carbon

THERE has recently been in this journal some discussion on the heat of dissociation of carbon monoxide<sup>1</sup>. In the most recent communication, Brons<sup>1</sup> states that the value for  $D_{CO}$  is definitely 8.41 volts = 193.9 kcal. It is the object of this letter to point out that the value given by Brons is not absolutely definite, and that there is still another possible value for this quantity, which up to now cannot definitely be excluded and is perhaps even more probable than the value given by Brons.

By a well-known procedure, the heat of sublimation  $L$  of carbon may be derived immediately from the heat of dissociation of CO, the heat of combustion of solid carbon to CO (26.4 kcal.) and the heat of dissociation of oxygen (116.4 kcal.). The value obtained with Brons'  $D_{CO}$  is  $L = 109.3$  kcal., whereas the value obtained from thermal data (vapour pressure curve of carbon) is  $L = 143$  kcal. This discrepancy, as was pointed out to me some time ago by Prof. P. Harteck, seems to be rather too large, and one is tempted to look for a loop-hole in the proof given by Brons.

Actually the value given by Brons is obtained from a new predissociation limit, 9.66 volts above the ground state of CO. The difference in energy of this limit from the limit found at 11.05 volts is just equal to the difference in energy of the  $^3S$  and  $^1D$  states in the carbon atom. The agreement is in fact rather close. However, as I have already pointed out on several occasions<sup>2</sup>, the actual dissociation limit may lie more or less below the predissociation limit, except in the cases where a breaking off of the rotational fine structure is observed for at least two successive vibrational levels. The latter is the case for the 11.05 volts limit in CO, and this limit is therefore a real dissociation limit; whereas for the new predissociation limit the breaking off has been observed for only one vibrational level, and therefore the value 9.66 is up to now only an upper limit to the corresponding dissociation limit, which in fact may be appreciably lower. Therefore the products

of dissociation at the upper dissociation limit (11.05 volts) need not necessarily be  $C(^3S) + O(^3P)$ , as concluded by Brons, but may also be  $C(^3P) + O(^1D)$ , assuming that the above-mentioned agreement is a chance coincidence. On this assumption, it follows that the heat of dissociation of CO is

$$D_{CO} = 73,760 \text{ cm.}^{-1} = 9.093 \text{ volts} = 209.7 \text{ kcal.}$$

The lower point of predissociation newly found by Brons would then correspond to a dissociation into normal atoms ( $C(^3P) + O(^3P)$ ) with 0.57 volts of excess kinetic energy. The comparatively large amount of excess kinetic energy is not unusual; for example, the predissociation of CO found by Schmid and Gerö<sup>3</sup> 0.48 volts above the 11.05 limit definitely leads to the same dissociation products as the 11.05 limit itself, that is, the atoms in this case have an excess kinetic energy of 0.48 volts. (This follows from the fact that the difference of the two predissociation limits, 0.48 volts, is definitely smaller than any plausible energy difference of the separated atoms.)

Our conclusion is therefore that, besides the value  $D_{CO} = 8.41$  volts = 193.9 kcal. given by Brons, the value  $D_{CO} = 9.093$  volts = 209.7 kcal. is also compatible with the predissociation data of CO now available. The latter value has the advantage that it does not lead to so low a value for the heat of sublimation of carbon. The value yielded is now  $L = 125.1$  kcal. instead of 109.3 kcal. (Incidentally, it may be remarked that the value of  $L$  obtained from  $D_{CO}$  is the heat of sublimation into normal atoms, not into molecules or a mixture of both, as the thermal value 143 kcal. (cf. above) probably is.) Furthermore, the heat of dissociation of the CN molecule into normal atoms obtained from the heat of sublimation of carbon, the heats of combustion of  $(CN)_2$ <sup>4</sup> and of carbon, the dissociation energy of  $N_2$  and that of  $(CN)_2$  into two CN<sup>5</sup> turns out to be 5.45 volts = 125.5 kcal. on the assumption of Brons. This is also improbably low, whereas the value  $D_{CO} = 9.093$  volts leads to  $D_{CN} = 6.17$  volts = 142.4 kcal., which seems more probable.

		Brons	Herzberg
$D_{CO}$	kcal. volts	193.9 8.41	209.7 9.093
$L$	kcal.	109.3	125.1
$D_{CN}$	kcal. volts	124.6 5.40	142.4 6.17

The two alternative sets of values are compared in the table above. A final decision between the two may only be obtained if more data on the predissociation of CO or CN, or on the heat of sublimation of carbon, are available. It may, however, be stressed that the accuracy of each set is rather high.

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<sup>1</sup> P. Goldfinger and W. Lasareff; B. Rosen, *NATURE*, **135**, 1077 (1935); H. Lessheim and R. Samuel, *NATURE*, **136**, 606 (1935); F. Brons, *NATURE*, **136**, 796 (1935).

<sup>2</sup> G. Herzberg, *Ann. Physik*, **15**, 677 (1932); G. Herzberg and H. Sponer, *Z. phys. Chem.*, **B**, **26**, 1 (1934); G. Büttenbender and G. Herzberg, *Ann. Physik*, **21**, 577 (1935).

<sup>3</sup> R. Schmid and L. Gerö, *Z. Phys.*, **96**, 546 (1935).

<sup>4</sup> J. McMorris and R. M. Badger, *J. Amer. Chem. Soc.*, **55**, 1952 (1933).

<sup>5</sup> G. B. Kistiakowsky and H. Gershinowitz, *J. Chem. Phys.*, **1**, 432 (1933).