

spectrophotometric method was used to observe the extent of adsorption.<sup>3</sup>

To determine the effect of proteolytic enzymes on the dye-coated substrate at high dilutions, a new method was developed for measuring proteolytic activity.<sup>4</sup> Klotz<sup>5</sup> has shown that denaturing agents such as heat or strong alkali, will cause the bovine serum albumin molecule to gradually lose its binding capacity for simple dye anions. We found that proteolytic enzymes had the same effect on the protein molecule. Thus, the action of the enzymes was followed by the change in the spectral property of the dye.

This spectral method was found so sensitive that the effect of one part per billion of pepsin upon the albumin molecule could be observed. However, when a coated albumin molecule having more than 200 dye anions on its surface was used as the substrate, even a concentration as high as 0.1% pepsin had no effect. When the substrate molecule contained less than a hundred dye anions, the substrate could be attacked and made to lose its binding capacity completely for dye anions. Thus, the incomplete unimolecular layer offered very little protection to the substrate.

The thickness of the "blanket" which inhibits the proteolytic action of pepsin on bovine albumin is a few Å. units. In view of these results, Rothen's interpretation of his experimental data is open to question.<sup>6</sup>

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(3) Klotz, *THIS JOURNAL*, **68**, 2299 (1946).

(4) Carroll, *Science*, in press.

(5) Klotz, *THIS JOURNAL*, **70**, 2935 (1948).

(6) Two points of criticism have been raised by the reviewer: (1) does a unimolecular layer form or do the dye molecules cluster about "certain sites," (2) is not the cessation of enzymatic activity, due to the conversion of the substrate from a positively to a negatively charged particle.

In answer to the first point, it may be stated that adsorption in 0.01 *M* hydrochloric acid appears to be a two-step process. Within one minute after the mixing of dye and albumin about 100 to 130 dye anions (of diversified structures) are taken up by a single albumin molecule. Since there are 110 cationic groups per protein molecule it is reasonable to assume that these groups are the loci of attachment for the dye anions. Further uptake of dye is more deliberate. Aging for several weeks was required to attain a coating of 250 dye anions. Whether these additional dye molecules take up vacant places on the surface of the albumin or whether two dye molecules cluster about every one of the 110 sites does not change the argument very much in favor of the existence of a unimolecular layer.

In regards to the question of the charge of the substrate, it would appear that the very criticism would be an additional reason why complex formation between enzyme and substrate is required for enzymic activity. It may be mentioned that the pepsin-albumin reaction has a half life of eight minutes<sup>4</sup> even when the system is at a pH 5.4. However the strongest argument that steric and not electrostatic effects are responsible for the cessation of enzymic activity will be published shortly. In this work the inhibiting effect of equivalent numbers of different dye anions on the surface of an albumin molecule are compared.

## Further Applications for Egloff's Boiling Point Equation

BY W. D. ENGLISH AND R. V. V. NICHOLLS

In our investigations of the hydrides of Group IV elements we were interested in deriving boiling point relationships. Because of similarity to hydrocarbons, Egloff's equation was considered.<sup>1</sup>

$$T = a \ln(n + b) + k$$

$T$  is b. p. in °K.,  $n$  is the number of central (carbon) atoms, and  $a$ ,  $b$  and  $k$  are empirical constants.

Previous investigators found that  $a$  and  $b$  were constant for all hydrocarbons except for widely varying structures,<sup>2</sup> while  $k$  varied with structure.

The classes of compounds investigated were the silanes, germanes, mono-*n*-alkyl silanes (terminal Si) and poly-*n*-alkyl silanes (internal Si). There were two different structural types for the poly-*n*-alkyl silanes (Tables V and VII).

We have found that equations similar to those developed by Egloff for the hydrocarbons are valid for these other series. The new equations (Tables II, III, IV, V and VII) show a root mean square deviation of the observed from the calculated boiling points of 0.68°, compounds in parentheses being omitted.

The tables include for comparison abstracts of two tables (nos. I and VI) from Egloff's paper.<sup>1</sup> It may be seen from Tables I, II and III that compounds which contain only one central atom have a practically constant deviation of -18° from the calculated boiling point. In Table VIII is a comparison of the various values of  $a$ ,  $b$  and  $k$  for the different series of compounds:  $k$  has the value -416.3 for all normal compounds and -424.5 for iso compounds;  $a$  and  $b$  vary from class to class, but have the same values when confined to different structures of the same class. Note the very similar values of  $a$  and  $b$  for the two classes of normal alkyl silanes.

As the values reported for  $a$  and  $b$  were calculated from a small number of compounds in most cases, they may be changed slightly when more compounds become known. However, the good agreement between calculated and experimental boiling points indicated the constants are close to their true values.

TABLE I

ALKANES<sup>1</sup>

$$T = 323.73 \ln(n + 4.4) - 416.31$$

Name	No. central atoms	$T$ , °K.		$\Delta T$
		Obsd.	Calcd.	
(Methane)	(1)	(111.55)	(129.63)	(-18.08)
Ethane	2	184.6	184.6	0.0
Propane	3	230.9	231.6	-0.7
Butane	4	272.6	272.7	-0.1

<sup>1</sup> Abstracted from Table 2, ref. (1).

(1) Egloff, Sherman and Dull, *J. Phys. Chem.*, **44**, 730 (1940).

(2) Corbin, Alexander and Egloff, *Ind. Eng. Chem.*, **38**, 156 (1946).

TABLE II  
SILANES

$$T = 395.8 \ln(n + 3.5) - 416.31$$

Name	No. central atoms	T, °K.		ΔT
		Obsd.	Calcd.	
(Silane)	(1)	(161.6) <sup>1</sup>	(179.0)	(-17.4)
Disilane	2	258.4 <sup>2</sup>	258.4	0.0
Trisilane	3	326.2 <sup>3</sup>	324.6	+ 1.6
Tetrasilane	4	381.2 <sup>4</sup>	381.2	0.0

<sup>1</sup> B. p. -116°, Adwentowski and Drozdowski, *Bull. inter. acad. sci. Cracovie*, (A) 330 (1911) (from *C.A.*, 6, 1722 (1912)); b. p. -112°, Stock and Somieski, *Ber.*, 49, 111 (1916); b. p. -111.9°, Stock, "The Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; b. p. -111.8°, Johnson and Isenberg, *THIS JOURNAL*, 57, 1349 (1935); b. p. 161.95°K., Stockland, *Kgl. Norske Videnskab-Selskabs*, Forh 12, 122 (1939) (from *C. A.*, 35, 2380 (1941)); b. p. -112°, Hurd, *THIS JOURNAL*, 67, 1545 (1945); b. p. -111.9° (781 mm.), Finholt, Bond, Wilzbach and Schlesinger, *ibid.*, 69, 2692 (1947). <sup>2</sup> B. p. -15°, Stock and Somieski, *Ber.*, 49, 111 (1916); b. p. -14.5°, Stock, "The Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; b. p. -19°, Johnson and Isenberg, *THIS JOURNAL*, 57, 1349 (1935); b. p. 259.0°K. Stockland, *Kgl. Norske Videnskab-Selskabs*, Forh 12, 122 (1939) (from *C. A.*, 35, 2380 (1941)). <sup>3</sup> B. p. 53°, Stock and Somieski, *Ber.*, 49, 111 (1916); b. p. 53.2° (766 mm.), Stock, Stiebeler and Zeidler, *ibid.*, 56, 1695 (1923); b. p. 52.9°, Stock, "The Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933. <sup>4</sup> B. p. 80-90° dec., Stock and Somieski, *Ber.*, 49, 111 (1916); b. p. ca. 109°, Stock, Stiebeler and Zeidler, *ibid.*, 56, 1695 (1923); b. p. 109°, Stock, "The Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933; b. p. 107.4°, Emeléus and Maddock, *J. Chem. Soc.*, 1131 (1946).

TABLE III  
GERMANES

$$T = 446.1 \ln(n + 3.0) - 416.31$$

Name	No. central atoms	T, °K.		ΔT
		Obsd.	Calcd.	
(Germane)	(1)	(183.0) <sup>1</sup>	(202.1)	(-19.1)
Digermane	2	302.2 <sup>2</sup>	301.7	+ 0.5
Trigermane	3	383.7 <sup>2</sup>	383.0	+ 0.7

<sup>1</sup> B. p. -91 to -90°, Schenk and Imker, *Ber.*, 58B, 271 (1925); b. p. -88.5°, Paneth and Rabinowitsch, *ibid.*, 58B, 1138 (1925); b. p. 184.80°K., Clusius and Faber, *Z. physik. Chem.*, 51B, 352 (1942). <sup>2</sup> Dennis, Corey and Moore, *THIS JOURNAL*, 46, 657 (1924).

TABLE IV  
MONO-*n*-ALKYL SILANES

$$T = 321.1 \ln(n + 5.2) - 416.3$$

Name	No. central atoms	T, °K.		ΔT
		Obsd.	Calcd.	
Methylsilane	2	216.3 <sup>1</sup>	216.4	-0.1
Ethylsilane	3	259 <sup>2</sup>	259	0
<i>n</i> -Propylsilane	4	296 <sup>2</sup>	296	0
<i>n</i> -Butylsilane	5	328 <sup>2</sup>	329	-1

<sup>1</sup> Stock and Somieski, *Ber.*, 52, 695 (1919). <sup>2</sup> Finholt, Bond, Wilzbach and Schlesinger, *THIS JOURNAL*, 69, 2692 (1947).

The compounds listed in Tables V and VII belong to the same class, (poly-*n*-alkyl silanes) and were therefore used together to calculate the values of *a* and *b* in these two tables.

Values for normal compounds are given in Tables I-V and values for iso compounds in Tables VI-VII. Compounds in parentheses in the tables were not used in calculation of the constants.

TABLE V

*n*-POLYALKYL SILANES

$$T = 322.0 \ln(n + 5.0) - 416.3$$

Name	No. central atoms	T, °K.		ΔT
		Obsd.	Calcd.	
Dimethylsilane	3	253 <sup>1</sup>	253	0
Dimethylsilane	5	327 <sup>2</sup>	325	+2
Di- <i>n</i> -propylsilane	7	384 <sup>3</sup>	384	0

<sup>1</sup> Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VI, London, Longmans, Green and Co. <sup>2</sup> B. p. 56° (741 mm.), Whitmore, Pietrusza and Sommer, *THIS JOURNAL*, 69, 2108 (1947); b. p. 54° (calcd.), Finholt, Bond, Wilzbach and Schlesinger, *ibid.*, 69, 2692 (1947). <sup>3</sup> Finholt, Bond, Wilzbach and Schlesinger, *ibid.*, 69, 2692 (1947).

TABLE VI

2-METHYL ALKANES<sup>1</sup>

$$T = 323.73 \ln(n + 4.4) - 424.51$$

Name	No. central atoms	T, °K.		ΔT
		Obsd.	Calcd.	
(2-Methylpropane)	(1)	(260.9)	(264.5)	(-3.6)
2-Methylbutane	5	300.93	300.88	+0.05
2-Methylpentane	6	333.43	333.59	-0.16
2-Methylhexane	7	363.23	363.32	-0.09

<sup>1</sup> Abstracted from Table 3, Ref. (1).

TABLE VII

DIMETHYL-*n*-ALKYL SILANES

$$T = 322.0 \ln(n + 5.0) - 424.5$$

Name	No. central atoms	T, °K.		ΔT
		Obsd.	Calcd.	
Trimethylsilane	4	283 <sup>1</sup>	283	0
Dimethyl- <i>n</i> -propylsilane	6	347 <sup>2</sup>	347	0

<sup>1</sup> Taylor and Walden, *THIS JOURNAL*, 66, 842 (1944). <sup>2</sup> Price, *ibid.*, 69, 2600 (1947).

TABLE VIII

CONSTANTS FOR THE EQUATION  $T = a \ln(n + b) + k$ 

Type of compound	<i>a</i>	<i>b</i>	<i>k</i>
Normal			
<i>n</i> -Alkanes <sup>1</sup>	323.73	4.4	-416.31
Silanes	395.8	3.5	-416.31
Germanes	446.1	3.0	-416.31
Mono- <i>n</i> -alkyl silanes	321.1	5.2	-416.3
<i>n</i> -Polyalkyl silanes	322.0	5.0	-416.3
Iso			
2-Methyl alkanes <sup>1</sup>	323.73	4.4	-424.51
Dimethyl- <i>n</i> -alkyl silanes	322.0	5.0	-424.5

<sup>1</sup> Ref. (1).

Egloff's equation was shown not to fit the boiling points of the hydroboranes, a result which is not surprising, considering the widely different basic structure.

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