THE ATOMIC WEIGHT OF YTTERBIUM

YbCl₃, g.	Ag, g.	YbCl₃: 3Ag	At. wt. of Yb	AgCl, g.	YbCl₃: 3AgCl	At. wt. of Yb
3.87107				5.94071	0.649934	173.108
3.82762				5.88965	.649889	173.089
4.12899	4.78127	0.863576	173.117	6.35269	.649959	173.119
2.58325	2.99157	.863510	173.095	3.97473	.649918	173.101
2.66672	3.08799	.863578	173.117	4.10299	.649946	173.113
2.58988	2.99916	.863535	173.104	3.98478	.649943	173.112
2.06819	2.39519	.863476	173.085			
2.42097	2.80349	.863556	173.100	3.72495	.649934	173.108
2.08411	2.41356	.863500	173.092	3.20680	.649904	173.095
1.72464	1.99732	.863477	173.085	2.65378	.649881	173.085
3.12912	3.62361	.863537	173.089	4.81490	.649883	173.086
3.92599	4.54636	.863546	173.107	6.04062	.649932	173.107
4.98554	5.77369	.863493	173.090	7.67151	.649877	173.083
	Average	.863526	173.098		.649916	173.100

higher value is evidently to be preferred although Wahl[12] by determination of isotopic abundances obtains the lower figure.

Mass	168	170	171	172	173	174	176
Per cent.	0.06	4.21	14.26	21.49	17.02	29.58	13.38

(12) Wahl, Naturwiss., 29, 536 (1941).

Lead.—Permyakov[13] finds the atomic weight of lead from Khito-Ostrov uraninite to be 206.12 and that from Sadon galena to be 207.20.

(13) Permyakov. Bull. acad. sci. U. R. S. S., Classe sci. chim., 581 (1941).

Mechanism of the Steam–Carbon Reaction[1]

BY B. R. WARNER[2]

It has been generally accepted that when steam is passed over carbon, the oxide of carbon first formed is principally carbon monoxide, and that carbon dioxide is formed mainly in subsequent catalytic reactions tending to establish the water–gas equilibrium

$$CO + H_2O \xrightleftharpoons[\text{catalyst}]{} CO_2 + H_2 \qquad (1)$$
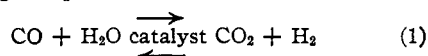
Most experimenters[3] base this conclusion on the observation that in all cases where steam velocity is so high that the equilibrium is not established, the experimental equilibrium constant, $p_{CO}p_{H_2O}/p_{CO_2}p_{H_2}$,[4] exceeds the true constant; that is, it

(1) Published by permission of the Director, Bureau of Mines, United States Department of the Interior. Not copyrighted.

(2) Associate Physical Chemist, Central Experiment Station, Bureau of Mines, Pittsburgh, Pa.

(3) Clement and Adams, Bureau of Mines Bull., 7, 50 (1911); Gwosdz, Z. angew. Chem., 31, 137 (1918); Taylor and Neville, THIS JOURNAL, 43, 2055 (1921); Pexton and Cobb, Gas J., 163, 160 (1923); Dolch, Gas u. Wasserfach., 175, 807 (1932); Terres and co-workers, ibid., 77, 703 (1934); Mayers, THIS JOURNAL, 56, 1879 (1934).

(4) This formulation of the equilibrium constant follows the convention of writing the exothermic reaction equation, CO + H₂O → CO + H₂ + 9646 calories and dividing the products of the concentrations on the left by the products of the concentrations on the right. By this convention the equilibrium constant of any reaction increases with temperature.

appears that the equilibrium is approached from the left. This conclusion assumes that at high steam velocities (i. e., short contact times) the gases leave the interstices of the carbon bed (where close contact with catalytic surfaces attains) before reaction (1) can proceed to equilibrium. Alternatively at high steam velocities steam may be channeled past the coal bed (such channels may exist or be formed during the reaction by erosion of the coke surface) without sufficient participation in the reaction. In this case it would be possible that equilibrium is established in the interstices, but the values of the experimental constant are high because the exit gas is diluted with steam. But if this were true, it would also follow that the ratio of CO_2/CO should remain constant with increasing steam velocities, if the reaction products were simply diluted with steam. However, in experiments with high steam velocities the ratio of CO_2/CO is found not to be constant but actually to decrease with increase in steam velocity. Thus the channeling effect is ruled out as the sole cause of the high values of the experimental equilibrium constant,

since the exit gas is not changed simply by dilution. Moreover, in this non-equilibrium state the ratio should vary with increasing steam velocities as follows: increase, if carbon dioxide is the primary product, and decrease, if carbon monoxide is the primary product. As stated above, the ratio decreases corresponding to a more rapid removal of the primary product, carbon monoxide, from the catalytic zone of the coal bed. The primary formation of carbon monoxide is further corroborated by experiments in which secondary reactions were prevented by passing steam over a carbon surface at very low pressures.[5,6] The attainment of the water-gas equilibrium depends on the nature of the catalytic surface of the coke and the time of contact (i. e., steam velocity).
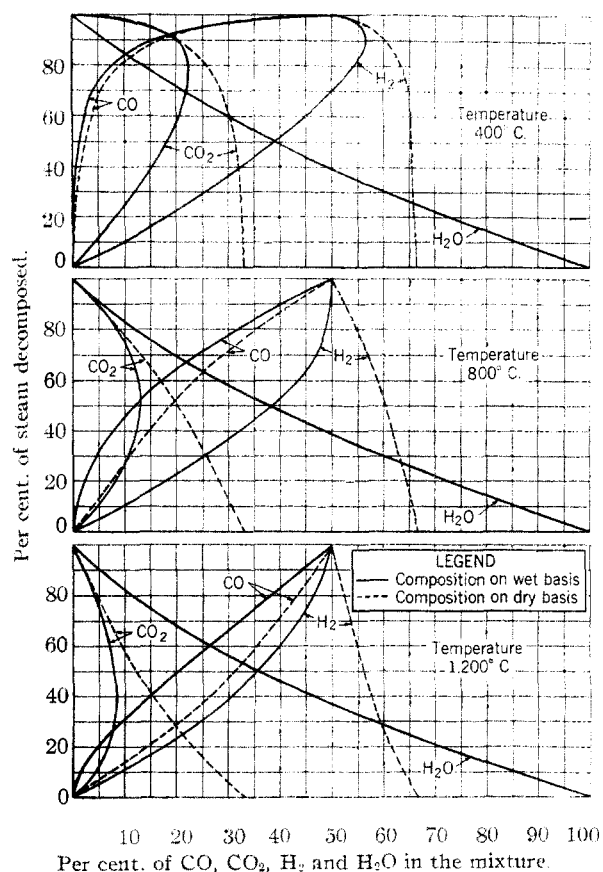

Fig. 1.—Gas composition in the steam-carbon reaction, calculated from the water-gas equilibrium at various temperatures for varying percentages of steam decomposed.

(5) Meyer, Trans. Faraday Soc., **34**, 1056 (1938); Sihvonen, Brennstoff-Chem., **17**, 281 (1936); Trans. Faraday Soc., **34**, 1062 (1938); Fuel, **19**, 35 (1940).

(6) Small amounts of carbon dioxide found by Sihvonen on preheating the water vapor at circa 10^{-4} mm. to 1100° may be attributed to the water dissociation, which in equilibrium attains several per cent.

A number of catalysts have been studied that accelerate, more or less selectively, the rate of gasification and the establishment of the water-gas equilibrium.[7] It is important to note that coke ash itself is a catalyst, particularly in wood charcoal and lignite char,[8] though its effect is more readily observable in the establishment of the water-gas equilibrium than on the rate of gasification. Furthermore, the structure of the carbon, as modified by carbonizing temperatures, and surface changes produced by various means influence the rate of gasification.

Although, as outlined above, the general mechanism is well established, kinetic problems remain, particularly concerning the rate of gasification. The subsequent reactions leading to water-gas equilibrium are of less interest, because with cokes used ordinarily, the equilibrium is rapidly established, a fact that permits rather accurate computation of the composition of the exit gas from knowledge of the reaction temperature and the percentage of steam decomposed (Fig. 1). On this basis the extensive data of Brewer and Reyerson[9] were analyzed. In the first place, Table I shows that the water-gas equilibrium is closely approached. The deviations between calculated and theoretical constants are not larger than may be expected from the uncertainties of temperature measurements and wet-gas analyses. Terres and co-workers[3] obtained similar results with cokes of this type. The problem of obtaining high concentrations of a desired product like hydrogen, which was the object of Brewer and Reyerson's work, is thus fully answered by the curves of Fig. 1. The dry gas approaches $66^2/_3\%$ of hydrogen and $33^1/_3\%$ of carbon dioxide at small percentages of steam decomposition, that is, at high steam velocities[10]; and 50% of hydrogen and 50% of carbon monoxide for complete decomposition, that is, at low steam velocities. High temperatures favor carbon monoxide, and low temperatures, carbon dioxide. The kinetic problem is concerned only with the rate at which carbon enters the gas phase,

(7) Cobb and co-workers, Gas J., **175**, 882 (1926); **179**, 548 (1927); **178**, 895 (1927); **182**, 946 (1928); Kröger and co-workers, Z. anorg. Chem., **197**, 321 (1931); **212**, 269 (1933); Z. angew. Chem., **52**, 129 (1939); Brennstoff-Chem., **19**, 157, 257 (1938); Z. Elektrochem., **44**, 524 (1938). Cf. Taylor and Neville, THIS JOURNAL, **43**, 2055 (1921); White and co-workers, Ind. Eng. Chem., **23**, 259 (1931); **26**, 83 (1934).

(8) Gwosdz, Dolch and Terres (ref. 3).

(9) Brewer and Reyerson, Ind. Eng. Chem., **26**, 734 (1934).

(10) It is, therefore, difficult to draw from these facts significant conclusions concerning the primary reaction (Scott, Ind. Eng. Chem., **33**, 1279 (1941)).

that is, with the total rate of formation of both oxides of carbon. If in a series of runs at constant temperature this rate is plotted against the final pressure of steam in the exit gas, the curves of Fig. 2 are obtained. It is noted that the total pressure in these experiments is one atmosphere; hence, the partial pressure of the steam decreases along the coal bed from one atmosphere to the final pressures plotted in Fig. 2. The latter increase with steam velocity owing to the decrease of the fraction of steam decomposed. The significance of these curves lies in their obvious tendency to flatten out; that is, there appears to be at any temperature a saturation pressure of steam above which the rate of gasification becomes constant. Thus, steam velocity influences rate of gasification only in the range in which saturation pressure has not been attained everywhere along the coke bed.
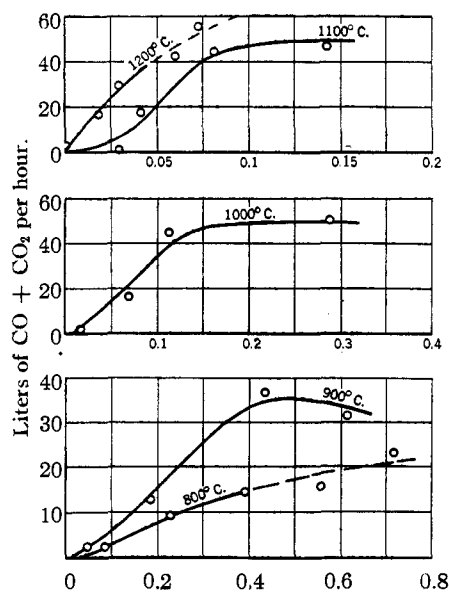
Partial pressure of steam (in atmospheres) at the outlet of the reaction tube.

Fig. 2.—Rate of gasification of lignite char in steam at various steam velocities and temperatures (data of Brewer and Reyerson).

It appears probable that such saturation pressures exist for all types of carbon, their value depending on the nature of the carbon and the temperature. Figure 3 illustrates the probable general relationship between rate of gasification and steam pressure at a constant temperature; such a curve conforms to the theory that the rate is governed by the amount of adsorbed steam in equilibrium with the vapor phase and becomes

TABLE I

WATER–GAS EQUILIBRIUM IN THE EXIT GAS FROM THE STEAM-LIGNITE CHAR REACTION

Data of Brewer and Reyerson. All runs under total pressure of one atmosphere.

Temp., °C.	Steam rate, moles/ hr.	Wet-gas analyses, %				K, calcd.	K, theor.[11]	Steam decomposed, %
		H_2O	CO_2	CO	H_2			
600	0.172	46.7	12.6	4.2	32.0	0.49	0.376	40.7
	0.885	81.7	5.5	0.3	11.7	.38		12.5
	1.917	85.4	4.3	0.2	9.3	.43		9.8
700	0.211	32.1	14.3	11.7	39.2	.67	0.515	55.0
	0.736	42.5	13.9	7.1	34.4	.63		44.7
	3.458	78.9	6.3	0.7	13.3	.66		14.4
	8.583	89.1	3.5	0.2	6.9	.74		7.2
800	0.172	8.7	4.7	37.4	42.8	1.62	0.916	83.1
	0.861	23.0	12.8	18.6	43.7	0.77		65.5
	2.094	39.4	13.6	9.8	35.5	.80		47.4
	3.478	55.8	10.8	4.4	26.4	.86		32.1
	8.606	71.9	8.3	1.1	18.1	.53		20.1
900	0.118	4.7	2.6	43.5	41.4	1.9	1.26	89.8
	1.019	18.5	9.5	25.3	42.2	1.2		69.5
	5.907	43.5	11.8	9.7	33.3	1.1		43.4
	8.803	61.1	9.9	3.7	22.6	1.0		27.0
1000	0.112	1.5	0.6	46.0	41.6	2.8	1.68	96.5
	0.917	6.8	4.1	39.8	44.5	1.5		86.8
	2.950	11.1	5.9	33.8	43.6	1.5		79.8
	5.800	28.9	10.6	17.9	35.1	1.4		54.8
1100	0.098	0.3	0.3	46.9	44.3	1.1	2.11	99.1
	0.928	4.2	1.9	44.7	44.4	2.2		91.3
	2.513	8.2	4.2	38.6	44.6	1.7		84.5
	3.461	14.3	4.5	32.5	38.5	2.7		72.9
1200	0.142	0.0	0.2	48.7	47.0	...	2.51	100.0
	0.980	1.8	0.8	46.1	44.6	2.3		96.1
	1.619	3.0	1.3	45.2	44.2	2.4		93.7
	3.042	6.1	2.7	42.6	44.0	2.2		87.8
	4.316	7.3	3.0	39.7	43.0	2.3		85.5

constant when the surface is completely covered. The theory implies that the temperature coefficient of the rate does not necessarily conform to the Arrhenius equation, as the rate is a function of both surface concentration and reaction probability in the adsorbed state. The data of Fig. 2, for example, show little difference in the rates at saturation pressures at 1000 and 1100°, suggesting that over this temperature range the effect of increase in reaction probability is diminished by the decrease of the surface concentration. At present, few experiments are reported
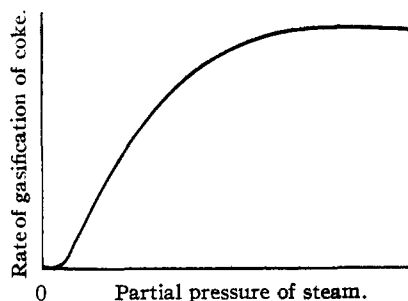

Fig. 3.—Probable type of curve of the rate of gasification of coke versus steam pressure.

(11) Lewis and von Elbe, "Combustion, Flames and Explosions of Gases," Cambridge Press, 1938, 382 pp.

in the literature that can be used to elaborate the theory further. Meyer[5] and Sihvonen[6] gasified graphite with steam at pressures of approximately 10^{-2} and 10^{-4} mm. and temperatures of 1400 to 2400°. Mayers[3] gasified graphite at atmospheric pressure and temperatures of 800 to 1200°. These investigators employed steam velocities great enough to ensure small percentages of steam decomposition. For equal graphite area, Mayers' gasification rates were much higher, namely, at 1000° already about 1000 times higher than those of either Meyer or Sihvonen at 2200°. In both Meyer's and Sihvonen's experiments the rate was found to be independent of steam pressure in apparent conflict with the high rates reported by Mayers. The facts can be reconciled by a type of adsorption curve found by Langmuir[12] for adsorption of carbon monoxide on glass, $x = b + ab_1p/(1 + ap)$, where x is the amount of gas adsorbed by a given weight of adsorbent, p is the partial pressure, and a, b, and b_1 are constants. If $p \to 0$, $x = b$, and the reaction is of zero order. This would correspond to Meyer's and Sihvonen's conditions. If, as may be true in Mayers' experiments, $ap \gg 1$, $x = b + b_1$, and, depending on the values of b_1 and b at 1000°, the rate is higher, its order is again zero, corresponding to the upper flat part of Fig. 3; but this has not been investigated experimentally.

Between the two extremes, $ap \simeq 1$, and the rate varies with pressure corresponding to the rising part of the curve of Fig. 3. Three samples of carbon have been studied by Thiele and Haslam[13] over a limited pressure range (300 to 1500 mm.). It appears that for one of their samples (steam-activated charcoal) the investigated range at 875° corresponds to the rising part of the curve close to the saturation pressure. For another sample (arc electrode carbon), the range at 1025° was probably in the linear part of the rising curve, whereas in the third sample (retort carbon), 1040 to 1125°, a new phenomenon appeared: the rate decreased with increase in steam pressure. Perhaps this is also noticeable in Brewer and Reyerson's experiments at 900° (see Fig. 2). The following explanation may be proposed: With increasing steam pressure, diffusion of the reaction products from the surface is impeded. Hence, they are adsorbed in competition with

steam, which is equivalent to surface poisoning. This poisoning effect may be attributable chiefly to carbon dioxide, which is more readily formed at higher steam pressures. More extensive work on the dependence of rate of gasification on steam pressure is indicated.

In the complete mechanism, several steps appear involved. First is the adsorption of steam, which is largely reversible and follows an adsorption isotherm of the Langmuir type. In part, the adsorption is irreversible, as was found by Muller and Cobb[14]; the steam cannot be recovered undecomposed. This may be due to activated adsorption in which the water molecules penetrate into the carbon lattice after overcoming an energy barrier, or to ordinary adsorption within localized strong fields of forces. The adsorbed steam is alternatively re-evaporated or transformed into an adsorption complex that decomposes into carbon monoxide and hydrogen. For the establishment of the water–gas equilibrium one may postulate another adsorption complex, which is formed either from water and carbon monoxide or from hydrogen and carbon dioxide and capable of decomposing into either set of products according to statistical probability. It is conceivable that this latter complex is adsorbed formic acid. If this is so, it may perhaps be desorbed to some extent and be detectable at low temperatures. Such experiments have not yet been reported. However, formic acid is known to decompose both ways on catalytic surfaces,[15] and its catalytic formation from hydrogen and carbon dioxide has been reported.[16] Similarly it is imaginable that the adsorption complex of the primary reaction is formaldehyde. There is evidence that carbon monoxide and hydrogen react in the presence of a catalyst to form formaldehyde[17]; and, furthermore, formaldehyde decomposes into hydrogen and carbon monoxide as well as water and carbon,[18] so that all the steps in the postulated primary reaction are in principle reversible. It is suggestive that sodium carbonate, which most effectively catalyzes the primary reaction between steam and carbon, also catalyzes the decomposition of formaldehyde into

(12) Langmuir, THIS JOURNAL, 40, 1389 (1918).

(13) Thiele and Haslam, Ind. Eng. Chem., 19, 882 (1927).

(14) Muller and Cobb, J. Chem. Soc., 177 (1940).

(15) Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford University Press, 1933, pp. 315, 357.

(16) Farlow and Adkins, THIS JOURNAL, 57, 2222 (1935).

(17) Chapman and Holt, J. Chem. Soc., 87, 916 (1905); Jahn, Ber., 32, 989 (1899).

(18) Tropsch and Roelen, Abhand. Kenntnis Kohle, 7, 15–36 (1925).

steam and carbon.[1a] This makes it appear that sodium carbonate catalyzes the formaldehyde-forming step: $C + H_2O \rightleftharpoons C(H_2O)_{ads.} \rightleftharpoons H_2CO$; according to this theory, sodium carbonate is a promoter for the catalytic activity of carbon, which by itself is able to decompose formaldehyde catalytically.[18] This mechanism for the acceleration of the steam–carbon reaction by sodium carbonate is in contrast to that of Kröger,[7] whose explanation involves a set of reactions completely divorced from the ordinary steam–carbon reaction.

Acknowledgment.—The author wishes to express his appreciation for the helpful criticism given by Dr. G. von Elbe, physical chemist, Central Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pa.
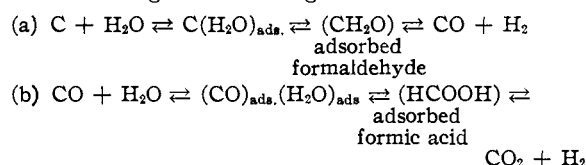
Summary

1. Interpretation of available data on the steam–carbon reaction corroborates the generally accepted conclusions that the primary products of the reaction are carbon monoxide and hydrogen

and that carbon dioxide is formed from the water-gas reaction which reaches or tends to reach equilibrium.

2. Available data suggest that the rate of gasification is governed by an adsorption isotherm for the steam and that a steam saturation pressure exists (its value depending on the carbon and the temperature), above which the rate of gasification at a given temperature becomes constant.

3. The nature of the intermediate adsorption complexes is discussed, the postulated reaction scheme being the following

(a) $C + H_2O \rightleftharpoons C(H_2O)_{ads.} \rightleftharpoons (CH_2O) \rightleftharpoons CO + H_2$
adsorbed
formaldehyde

(b) $CO + H_2O \rightleftharpoons (CO)_{ads.}(H_2O)_{ads} \rightleftharpoons (HCOOH) \rightleftharpoons$
adsorbed
formic acid
$CO_2 + H_2$

4. A theory for the catalysis of the steam–carbon reaction is offered.

An Electron Diffraction Investigation of Biphenylene

By Jurg Waser and Verner Schomaker

W. C. Lothrop[1] has synthesized an aromatic hydrocarbon $C_{12}H_8$ to which he assigns the structure (I) and the name biphenylene. It was thought worth while to establish the structure of Lothrop's biphenylene by other than chemical means. In this we have succeeded, mainly by the electron diffraction investigation described below. Our work confirms structure (I) and in particular rules out structure (II)

(I)   (II)
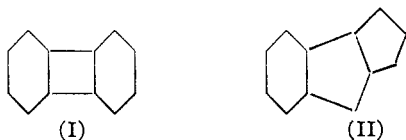
which has been proposed by W. Baker[2] and supported by C. A. Coulson.[3] Biphenylene and its derivatives synthesized by Lothrop are thus the first molecules of definitely established structure

(1) W. C. Lothrop, This Journal, **63**, 1187 (1941); **64**, 1698 (1942).
(2) W. Baker, *Nature*, **150**, 211 (1942).
(3) C. A. Coulson, *ibid.*, **150**, 577 (1942).

to contain the interesting aromatic four-ring. They should prove very valuable for studies of orientation effects due to conjugation and to strains of the bond angles (Mills–Nixon effect).

Our investigations were carried out with a 1.5-g. sample of the compound, kindly given to us by Dr. Lothrop.

Electron Diffraction Investigation

Procedure.—The electron diffraction investigation was feasible because of the relatively high vapor pressure of biphenylene. It was carried out with the use of the high temperature nozzle, which had to be heated to around 200°. The wave length of the electrons used, $\lambda = 0.0615$ Å. was determined by transmission pictures of gold foil ($a_0 = 4.070$ Å.). Of the sixty pictures which were taken at nozzle–film distances of about 10 or 20 cm., about a fifth showed satisfactory rings, some out to about $s = 25$ Å.[−1].

In principle, the problem of an electron diffrac-