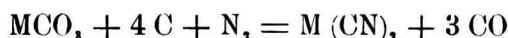


Chemistry. — “*Nitrogen fixation by means of the cyanide-process and atomic structure.*” By DR. L. HAMBURGER. (Communicated by Prof. P. EHRENFEST).

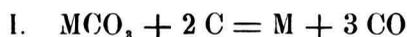
(Communicated at the meeting of June 30, 1923).

a. *Introduction.* It is known that the reaction



forms the foundation for the nitrogen fixation by the so called cyanide process. For this conversion the temperature at which the capture of the nitrogen takes place with practically appreciable velocity appears to be very divergent, according as another M is chosen for the metal. H. LUNDÉN¹⁾ has also included rubidium and cesium in his researches, and is of opinion that there is a relation between the boiling-points and atomic weights of the metals in question and the “cyanizing-temperature”. It is, however, not possible to derive a quantitative relation on this foundation.

b. *Stages of the cyanizingreaction.* In order to arrive at a clear insight the fact should be considered that according to J. E. BUCHER²⁾, two stages before all should be distinguished in the course of the reaction:



Of these reactions I bears an exceedingly endothermal character, II on the other hand, is strongly exothermal, II takes place practically momentarily (either with addition of a catalyst or without). Whether a practically appreciable reaction-velocity will appear, will therefore depend on I. The strongly endothermal character of I³⁾, however, causes the temperature to remain pretty well constant, when the reaction sets in, till the reaction of MCO_3 has been completed. The quantities of energy required for this are so great, that, especially at comparable conditions, factors like energy-quantities,

¹⁾ Cf. TH. THORSELL. *Zeitschr. f. angew. Chem.* **33**, 251 (1920).

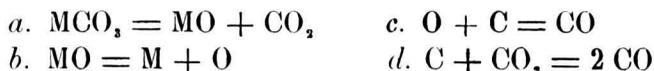
²⁾ J. E. BUCHER. *Jl. of Ind. and Eng. Chem.* **9**, 233 (1917).

³⁾ In consequence of which the total reaction I + II is also still endothermal in a high degree.

required for division, dilution, solution, melting and evaporation remain of subordinate importance ¹⁾. Hence notwithstanding the complicated character, we have to do with:

1. comparatively characteristic reaction temperatures;
2. with the decisive influence of metal-formations.

We can now divide I again into the following more elementary processes:



in which *c* and *d* follow the same reaction equation for all metal cyanide-syntheses, whereas *b* is first of all the reaction which claims the lion's share of the energy-supply.

c. The primary reaction. From W. KOSSEL's ²⁾ point of view the course of *b* means only this, that under the influence of the supplied energy in the metal oxide the oxygen cedes again the negative electron taken from the metal. In our case this view entails the difficulty that this restitution would have to take place more easily with metal atoms with relatively great affinity to the returning electron than to more electro-positive elements. In reality, however, the reaction appears to set in more easily with increasing electro-positivity of the elements.

It is, however, not necessary to assume that in every metal-metalloid compound one or more of the metal-electrons has quite gone over to the metalloid. In many cases it may be more a question of partial transition, i. e. conditions will be found in which only partial separation ("Lockerung", dislocation) of the metal- (valency-) electron with regard to the metal atom must be assumed. In connection with the spectral interpretations by BOHR this may also be expressed thus, that the electron in question will on an average be at the disposal both of the oxygen atom and of the metal atom in a characteristic "abnormal" path.

The decreasing reaction temperature with the increasing electro-positivity of the metal leads us further to the assumption that pri-

¹⁾ In the same way the dependence of the reaction-energy on the temperature may be neglected within a wide margin. The possibility of all these approximations stamps the cyanizing-reaction as one of the few chemical conversions, which like the rare ideal photo-chemical reactions are able to give experimentally demonstrable indications in favour of the theories which at the same time bear a fundamental and idealizing character [cf. e. g. F. WEIGERT, *Zeitschr. f. Phys.* **14**, 383 (1923)].

²⁾ W, KOSSEL, *Ann, d. Phys.* **49**, 229 (1919).

marily the electron does not entirely return to the metal atom, but that inversely a complete separation of the valency-electron from the metal rest should be taken into account. It is this process that we shall subject to a fuller examination in what follows, and which we shall briefly denote by the expression of "primary reaction".¹⁾

Hence we come to realize the possibility of the conclusion that the dissociation of the metal oxide does not take place by the direct process of splitting up $MO = M + O$, but that with increase of energy first an *activation* sets in, manifesting itself as formation of ions. From this activated condition the further course of the reaction takes place.

Thus we are led to place ourselves on the basis of these theories of reaction-velocities which have appeared to possess remarkable validity, at least in definite cases; particularly we come to the "activation" basis given as of general validity first by Sv. ARRHENIUS²⁾ and later among others by J. PERRIN³⁾ in his "Lumière et Matière".

d. Ionisation Potential.

It is known that the ionisation potential of the vapour is a decisive quantity for the detaching of an electron from a free metal atom. Where there is reason to assume that the primary reaction takes place in the gasphase⁴⁾ we will first of all try, in connection with the view about the primary reaction given under *c*, in how far the ionisation potential can also govern the cyanizing-reaction. For this purpose we will calculate the values of the quantity $\frac{V}{T}$ according to the table below, in which V represents the ionisation potential

¹⁾ A possible addition of the separated electron to the oxygen rest should be considered as a second stage. From J. FRANCK's researches on the collisions of slow electrons in electro-positive and noble gases we know that negative electrons are seized by oxygen, but are on the contrary under certain conditions relinquished by the electro-positive atom. In the same way a partially bound electron, which gets free through "critical" energy supply with small velocity [thus the lower limit of energy supply required to bring about the primary reaction may be indicated for brevity], may be bound to the oxygen atom. We leave this out of account in the next close examination of the primary reaction.

²⁾ Sv. ARRHENIUS. Zeitschr. f. Phys. Chem. **4**, 226 (1889).

³⁾ J. PERRIN. Ann. d. Phys. **11**, 5 (1919).

⁴⁾ All the metal carbonates or oxides of the alkalis and earth-alkalis are greatly or appreciably volatile at the indicated reaction temperatures. In the dissociable carbonates the evaporation is promoted by the formation of oxydes in molecular distribution (formation "in statu nascendi" and transportation by the gas current). The parallelism between the cyanizing temperature and volatility of the carbonates resp. oxydes is striking.

of the free alkali-resp. earth alkali atoms, and T the cyanizing-reaction-temperature.¹⁾ It is seen from the fourth row of the table that the same order of magnitude is found everywhere for $\frac{V}{T}$.

Row 1	Metal	Li.	Na.	K.	Rb.	Ce.	Mg.	Ba.	Sr.	Ba.
2	Reaction-temp. in °K(T)	1370	1200	1100	970	870	2100?	1900	1670	1320
3	Ionisation-potent. in volts (V)	5.4	5.1	4.3	4.2	3.9	7.6	6.1	5.7	5.2
4	$\frac{V}{T} \cdot 10^3$	4.2	4.2	4.0	4.2	4.3	3.2?	3.2	3.4	3.9
5	Excitation potential V'' in Volts	1.84	2.09	1.60	1.55	1.38	2.70	1.88	1.79	1.56
6	$\frac{V - V''}{T} \cdot 10^3$	2.5+	2.5	2.5-	2.7	2.86	2.3	2.2	2.3	2.7

Considering the widely divergent circumstances the agreement may even be called remarkable, the more so as a perfectly sharply defined reaction temperature cannot be expected on theoretical ground either.

e. Dislocation potential.

The ionisation potential determines the energy required to detach an "outer" electron of a metal atom entirely from a normal path. As under *c* we arrived at the view that in the compound the electron in question is present in an abnormal path, the conclusion is obvious that not V , but a smaller quantity $V - V'$ can give a measure for the critical supply of energy, in which V' is a quantity which determines the difference of energy between the electron in the abnormal path of the compound and the electron in the free metal atom, that is in the normal path. We shall call this quantity briefly dislocation potential, the electron in the abnormal path will be called dislocated electron.

The separation of the dislocated electron from the metal rest must, in our opinion, require a quantity of energy that is proportional to

¹⁾ The value of the reaction temperature of CaO is taken from a communication by P. SCHLÄPFER (Schweiz. Chem. 1919, Heft 29 (30), the values of the ionisation-potential are derived from a summary given by J. FRANCK (Phys. Zeitschr. 22, 413 ('21). The values of T taken for *Mg* and *Ca* will be discussed elsewhere, among others because reduction- and cyanizing-temperature (resp. the temp. of the formation of metal cyanamid) differ considerably for (the compounds of) these elements.

$e(V-V')$ (in which e represents the charge of the electron), and which is derived from the available thermal energy of the medium. Putting the latter in approximation proportional to T , we find:

$$e(V-V') = kT,$$

so that the following relation is found:

$$\frac{V-V'}{T} \text{ must be constant for all cyanizing reactions.}$$

f. Excitation potential.

With the analogous structure of the "outer electron shells" of the homologous elements it is probable that in the metal oxide the dislocated electron as a rule and on an average will be in a corresponding abnormal path. With the available data we can, however, not say which. When we, however, compare the values of the excitation tension V'' of the different elements, which quantity is decisive for the energy-supply required to transfer an "outer" electron in the metal atom from the normal into the first abnormal path (Row 5 of the table) with the ionisation potential (row 3), the analogous course of these values with increasing electro-positivity of the elements, is striking. When we, therefore, introduce the quantity $V-V''$ instead of $V-V'$ we should, reasoning in the same line, obtain practicable results not only for these cases in which the abnormal path of the valency electron in the compound would be identical with the first abnormal path, but also when the position of the dislocated electron would be identical with another abnormal path. A considerable difference between V'' and V' is, however, unlikely, because then the value of the quantity $V-V''$ would no longer be in accordance with the considerable energy-supply required if the primary reaction is to take place ¹).

In row 6 the values are recorded of the quantity $\frac{V-V''}{T} \cdot 10^4$.

It is seen that the difference between the alkalis and the earth alkalis is smaller than in row 4. Considerations for a further correction will be given elsewhere.

g. In conclusion we will remark that with the aid of RUTHERFORD-BOHR'S atomic model we have endeavoured in the above to

¹) This is the more cogent as moreover at the complete addition of the "outer" electron to the oxygen rest energy is liberated. We have not considered this more closely, because this increase of energy with regard to the oxygen rest may be put equal for all the metal oxydes considered, and can therefore not give occasion to characteristic differences. [See also "note at the correction"].

give an example of the view that at least in definite cases, ionisation- and dislocation-potentials are not only decisive with regard to the possibility of reaction, but also with regard to reaction velocity and reaction temperature.

PERRIN sees photo-chemical action in every chemical action. Our insight into the structure of the atom makes us realize that the fundamental feature is the displacement of the electrons in it. This displacement may be brought about by radiation, but also in various other ways. Accordingly it is not justifiable to assign merely a part to light in the explanation of chemical action; other forms of energy also make their influence felt. In connection with the conception of an interaction between the different forms of energy, the possibility might, however be considered of a derivation, even though it be a formal one, of the relation $\frac{\text{critical energy supply}}{\text{reaction temperare}} = \text{constant}$ from the laws of radiation, in which case the directing lines given by R. C. TOLMAN¹⁾ and E. K. RIDEAL²⁾ should be taken into account. This will be treated elsewhere.

Dordrecht, June 26th 1923.

Note at the correction. From recent determinations of the electron-affinity of some electronegative elements as well as from known electro-chemical data may be deduced — as will be shown elsewhere — that the addition potential of an electron to an atom of oxygen can at most be about 2 volt. This value confirms the assumptions given sub *f* and justifies the neglect of the addition potential of the valency-electron to the oxygen, the value of which in our cases (as a rule) can only be little.

July, 4th, '23.

¹⁾ R. C. TOLMAN. Journ. Amer. Chem. Soc. **42**, 2506 (1921).

²⁾ E. K. RIDEAL. Phil. Mag. **42**, 156 (1921).