

then occurred.¹⁵ The measured reaction rate on this basis would be proportional to the probability that an atom in the molecule vibrates sufficiently, to get beyond the range of molecular attraction. The temperature coefficient of the reaction velocity should then be proportional to the increase in intra-molecular vibration with temperature and the critical increment calculated from the observed rates, a measure only of the change in vibrational energy of an atom or atoms in the molecule due to change in temperature.

Summary

1. The decomposition of nitrogen pentoxide has been studied in presence of infra-red radiation between the limits 2μ and 8μ inclusive of the two absorption bands at 3.4μ and 5.8μ exhibited by the gas.

2. Although the degree of accuracy attained would not warrant a complete denial that no acceleration of the decomposition had occurred due to the infra-red radiation, it has been shown that no such marked effect as the simple radiation theory would suggest is noticeable.

3. A general discussion on the application of radiation to chemical reaction was presented with special reference to unimolecular reactions.

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A NEW METHOD FOR THE ELECTROLYTIC SEPARATION OF METALS

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A substitute for the auxiliary electrode used by Sand,¹ and later by others, in the separation of metals by electro-analysis is given in this paper.

A wire of the metal to be deposited is immersed in the solution from which the metal is to be deposited. This wire is connected to the cell, voltmeter, etc., in the same manner as is the auxiliary electrode used by Sand. The details of the methods used in the determinations are those given by Schoch and Brown² modified by the use of the wire for the auxiliary electrode. While the metal is being deposited on the cathode, the current is controlled so that the observed potential of the cathode ΔE , is -0.10

¹⁵ The distribution of the energy of vibration among the various molecules will presumably follow a normal Maxwellian curve and those with a high energy will be the first to decompose. How the Maxwellian distribution is to be restored does not appear any more evident than the restoration of the Maxwellian distribution among electrons between collisions, recently demonstrated by Langmuir [*Phys. Rev.*, **26**, 585 (1925)], unless it occurs by impact with quanta of radiation in some form.

¹ Sand, *J. Chem. Soc.*, **91**, 379 (1907).

² Schoch and Brown, *Trans. Am. Electrochem. Soc.*, **22**, 265 (1912). THIS JOURNAL, **38**, 1660 (1916).

to -0.20 volt in relation to this wire. The electrolyzing current is maintained until it reaches a residual value as in the deposition by the method of Sand. For metals such as bismuth, which have a tendency to deposit in a powdery form, the cathode potential, during the earlier part of the deposition, is kept somewhat less negative. The wire and the cathode are always weighed together.

When no wire of the metal is available, then a platinum wire, or for tin a copper wire is placed in parallel with the cathode and the current broken a moment before the wire is used as an auxiliary electrode. In each case where platinum wire is used in parallel a low potential difference must be used until the wire is covered with the deposited metal.

Only such separations have thus been attempted as were shown to be possible by earlier work and by the "single potentials" of the metals that were determined. No attempt was made to separate metals whose separation is admittedly easy. For those, as with the ordinary use of the auxiliary electrode, larger potential difference may be used for the separations.

TABLE I
REPRESENTATIVE RESULTS

Metal	Present, g.	Found, g.	ΔE	Other constituents of the solution
Copper	0.7554	0.7546	-0.20	Hydrochloric acid, hydroxylamine and stannous chloride
	.5660	.5666		
	.7940	.7934		
	.4600	.4604		
	.5512	.5508		
	.3692	.3694		
Bismuth	.2712	.2708	$-.10$	Hydrochloric acid, hydroxylamine and lead chloride
	.3085	.3092		
	.2987	.2986		
Antimony	.4127	.4124	$-.15$	Hydrochloric acid, hydroxylamine and stannous chloride
	.3365	.3360		
	.3482	.3480		
	.3490	.3496		
	.3460	.3465		
	.3862	.3858		
Tin	.4410	.4418	$-.10$	Hydrochloric acid, hydroxylamine and cadmium chloride
	.3518	.3514		
	.3508	.3510		
	.4026	.4022		
	.4240	.4234		

These results indicate that it is possible to substitute a wire of the metal that is being deposited for the reference electrode in separations in which the cathode potential is controlled.

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