This experiment is a very incomplete one and I should be glad to see further work (which I can not do myself at present) done on the uses of this interesting fluid.

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A NEW PROCESS FOR HANDLING SOUTH AFRICAN PLATINUM ORES

The *South African Mining and Engineering Journal* for September 8 and 15 gives a detailed description of a new process of platinum recovery from the sulfide-norite ores of the Transvaal, which has been originated in the Ferreira laboratory of the Rand Mines metallurgical department. As the process is along new lines, a brief outline is of general interest.

The ores, after crushing and ball-mill grinding, are reduced by flotation to a 5 per cent. concentrate. These concentrates contain, in addition to the platinum metals, copper and nickel sulfides and a small amount of gold. They are first roasted to a negligible amount of sulfur, then mixed with salt and heated with chlorine in a muffle. The temperature used is about 540° C., at which heat the platinum metals, as well as the copper and the nickel, are completely changed into soluble chlorides, while the temperature is too high for the chlorination of the gold. The current of chlorine is so controlled that practically all is absorbed, the amount used being 100 to 120 pounds per ton of concentrates. The platinum metals are changed into the very soluble sodium chloro-salts.

The chlorinated mass is leached with slightly acid water and the copper precipitated as the carbonate by finely ground limestone. This precipitate runs about 20 per cent. copper and can be smelted direct to blister copper. The small amount of platinum and iridium precipitated with the copper is recovered as anode sludge when the copper is electrolytically refined. After filtering from the copper precipitate, the platinum metals are precipitated by zinc dust, and after refiltering the solution is run through a zinc extractor for complete recovery of the platinum metals. The nickel present is then thrown down with bleaching powder. The chlorinated ore, after leaching, is treated by cyanidation for gold.

The novelty of the process consists in the chlorination of the platinum metals and the precipitation of the copper by limestone. The process has already passed beyond the laboratory stage, and works satisfactorily on semi-plant scale. It promises to be a solution of the difficult problem of handling the South African platinum ores.

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SPECIAL ARTICLES

SCATTERING OF QUANTA WITH DIMINUTION OF FREQUENCY

The purpose of this note is to point out the correlation of several recent experiments on scattering of quanta with one another and with a very general principle which was foreshadowed some years ago, and has since then become more plausible through the demonstration that quanta and electrons alike possess some of the qualities of waves.

The notable experiments of Raman, verified and extended by several other physicists,[1] have shown that a quantum of sufficient frequency impinging upon a molecule may employ some of its energy in exciting the molecule, and continue on its way with the remainder, rebounding from the impact in the form of a quantum of diminished energy and augmented wave-length. The analogy with the electron is very close, for an electron may use part of its energy in exciting an atom, and rebound from the encounter in the form of an electron of diminished energy and augmented wave-length. In addition, various experimenters[2] have shown that a quantum impinging on a crystal may spend part of its energy in exciting vibrations of the sort which are responsible for Reststrahlen, and which are attributed to inter-atomic forces of the lattice; and having done this, the quantum may emerge with the balance of its energy and a correspondingly modified wave-length.

In the Compton effect—to use this term in its restricted sense—a quantum confers upon a free or nearly free electron a fraction of its energy, and goes onward with the remaining fraction, its wave-length being altered accordingly. In a sense, this case is at the opposite extreme from that which Raman observed, for the transferred energy goes into a non-quantized form. Cases intermediate between these two extremes are disclosed by two recent series of experiments. In those of Davis and Mitchell,[3] the scattered X-rays emerging from carbon (in the form of graphite) irradiated by the $K\alpha_1$ rays of molybdenum were found to comprise quanta which are evidently incident quanta which have given up an amount of energy just sufficient to extract an electron from the K-level of a carbon atom. The wave-length of these agrees within 4 per cent., as the authors point out, with the value predicted from this interpretation. There are two other sets of scattered quanta

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[1] C. V. Raman and K. S. Krishnan, *Indian Jl. of Phys.*, March 31 and July 31 (1928); *Nature* (1928) *passim;* P. Pringsheim, *Naturwiss.*, August 3 (1928); R. W. Wood, *Nature*, Sept. 8 (1928).

[2] C. V. Raman, *ibid.;* G. Landsberg, L. Mandelstam, *Naturwiss.*, July 13 (1928).

[3] B. Davis and D. P. Mitchell, *Phys. Rev.*, 31: 1119; 32: 331–335 (1928).

which have lost amounts of energy agreeing in order of magnitude with the amounts required to extract superficial electrons from carbon atoms; and while Davis and Mitchell state that the agreement is not exact, the extraction-potentials of these superficial electrons are still so uncertainly known and so much influenced by the environment of the atom that we need not yet concede that there is a contradiction. Indeed, it might be contended that the displacements of these two sets of quanta from their initial frequency are the best extant measures of the extraction-potentials of the outer electrons of carbon atoms in the graphite lattice. In these experiments, then, quanta confer upon atoms sufficient energy to remove individual bound electrons, and are scattered with the energy they have left over. Other such cases are revealed by the great quantity of data obtained during the years 1923–24 by G. L. Clark, W. Duane and their collaborators,[4] bearing upon what they called the "tertiary radiation" of substances irradiated by X-rays. I am indebted to my colleague, Dr. C. H. Prescott, for an allusion to these in the course of a conversation about the "Raman effect."

This tertiary radiation is precisely analogous to the scattered quanta with diminished frequency observed in the X-ray region by Davis and Mitchell, and in the optical region by Raman. To show this it is sufficient to quote the theory originally propounded by Clark and Duane, which was found adequate to account for the *frequencies* though not for the *intensities* of the tertiary rays. They assumed that the primary quanta extract electrons (usually K electrons, in the conditions of their experiments) from the atoms on which they impinge, and that these electrons are suddenly retarded or arrested by impacts on other atoms, conferring their kinetic energy on newborn quanta by the same process as is supposed to occur when continuous-spectrum X-rays are generated by the impact of cathode-rays on the target of an X-ray tube. The quanta so created should have frequencies ranging upward from an unspecified minimum to a maximum equal to that of the primary quanta *minus* the K-excitation-frequency of the scattering atoms. Bands with short-wave-limits at the stated frequency were actually found in the spectra of X-rays scattered by silver, molybdenum, germanium and several other elements. Now exactly the same phenomena are to be foreseen if the "tertiary" quanta are primary quanta which have spent some of their energy in extracting K electrons from atoms and in endowing these with various quantities of extra kinetic energy. This theory, which was proposed by A. H. Compton,[5] does not seem to be endangered by the absolute intensities and the distribution-in-intensity of the observed bands, which according to D. L. Webster[6] were incompatible with the theory of Clark and Duane. The absolute intensities are measures of the abundance of quantum-impacts of this type; the distribution-in-intensity of any band depends upon the relative probabilities of the transfer of different amounts of kinetic energy to the liberated electrons.

We have thus at least four and perhaps five distinguishable cases of quanta surrendering part but not the whole of their energy: (1) in excitation of molecules (Raman); (2) in excitation of vibrations in crystal lattices (Raman, Landsberg and Mandelstam); (3) in collisions with free electrons (Compton); (4a) in ionization of atoms by removal of inner electrons, attended in general by transfer of additional energy to the liberated electrons (Duane and Clark); (4b) in ionization of atoms by removal of inner and outer electrons, not attended by additional transfer of energy to the liberated electrons (Davis and Mitchell). Probably, then, it is a valid general principle that a quantum can divide its energy, giving up a part and retaining the remainder; and this can happen whenever there is an encounter between a quantum and an electron, atom or system of atoms capable of receiving energy in quantities smaller than the quantum initially possesses. This principle was adumbrated by A. Smekal[7] before any of the experiments which I have cited. One wonders why it did not earlier win favor; but very likely the reason is that until very recently it has not been easy to conceive that a quantum may change its frequency and yet, in a profound sense, remain the same quantum. One felt instinctively that if a quantum of one frequency entered an atom or a piece of matter and a quantum of another frequency emerged, the former must first have disappeared, the latter have been subsequently born through some intermediate process. Now that it is clear that electrons also possess the properties of wave-motion, the difficulty becomes universal, and consequently acceptable. When an electron is speeded up or slowed down, its wave-length changes; if we conceive that nevertheless it remains the same electron, can we do otherwise than suppose that a quantum retains its identity when its wave-length is altered?

Of course it must not be supposed that whenever a quantum of one frequency strikes an atom and a quantum of another frequency comes off, there has been a scattering-process of the foregoing type. Certainly there are cases in which an atom absorbs a

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[4] *Proc. Nat. Acad. Sci.*, 9 (1923) and 10 (1924).

[5] *Phys. Rev.* (2), 24: 168–177 (1924).

[6] *Proc. Nat. Acad. Sci.*, 10: 186–191 (1924).

[7] *Naturwiss.*, 11: 873–875 (1923).

quantum and after an appreciable interval of time emits another, for it is known that a "collision of the second kind" may involve the atom before the interval is ended, and alter the character of the emitted quantum. This might be made the basis for the distinction between fluorescence and scattering.

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THE USE OF INTERNAL PRESSURE IN METALLIC SYSTEMS

System Lead-Antimony Copper

Until recently the application of thermodynamic relationships to metallic systems has been almost wholly neglected. J. Johnston,[1] using a method similar to that proposed by Washburn[2] and Read, has shown that the eutectic composition and temperature can be calculated from the solubility curves, and conversely, knowing the eutectic temperature, the solubility can be calculated. In this work, ideal solutions are postulated, but many metallic solutions must closely approach this condition, so that the method should be valuable as a first approximation.

There are three properties of metals which are useful in predicting the miscibility of the liquid phase or even hazarding a guess as to the solid solubility. The most important of these is the internal pressure which is defined by Dupre,[3] as equal to $(-T\frac{\alpha}{\beta})$, where "T" is the absolute temperature, α the coefficient of expansion, and β the coefficient of compression. Liquids with like internal pressures should be more easily miscible than those with unlike. That this assumption is at least followed in substance is demonstrated by Hildebrand[4] with a correlation of existing data on the subject. He shows that those metals which form continuous series of solid solutions have very similar internal pressures, and that those metals which display a miscibility gap are separated in the table by a definite amount. The other two useful properties of the metal are the melting-points and heats of fusion.

The formation of compounds may have a greater effect than the properties named above. The extent of the effect of the compound formation depends on the stability of the compound. When it is stable in the liquid phase, it must be considered a new component with its own internal pressure, melting-point and heat of fusion. On the other hand, compounds which dissociate completely at or before their melting-point have little effect on the miscibility of the liquid phase, since the liquid phase is then composed of only the two original metallic atoms. However, the compound may have a decided bearing on what solid will separate under a given set of conditions. In addition to the melting-points and heats of fusion, the heat of formation of the compound must be taken into consideration. The shape of the liquidus and solidus surfaces depends on these principles. With the help of certain judiciously chosen freezing curves, the surfaces may be accurately known.

Application to the Copper-Lead Antimony System

In studying the ternary system of lead-antimony copper,[5] there is a good chance to demonstrate the effect of internal pressure in shaping the liquidus surface. In building this surface it is important to have the component binary liquidus lines in mind. In the system lead-antimony[6] no compounds are formed, and there is a solid solubility of antimony in lead as well as a reported solid solubility of lead in antimony.[7] The eutectic occurs at 12.5 per cent. antimony. From Table I it is seen that the internal pressures of lead and antimony are close together. The value for bismuth is shown in the table because it is the only metal other than antimony in the fifth group of the Periodic Table for which any values could be found. General trends in the Periodic Table indicate that internal pressure decreases in going from top to bottom in any group, which places the value for antimony in the vicinity of that for lead. From this consideration,

TABLE I

Relative Internal Pressures

Metal	From expansion and compression of solid metals*	Heat of vaporization*	Surface tension*	Boiling points	Viscosity at 1100° C.†
	α/β	L/V	γ/v^3	°C.	η
Cu	67	8850	581	2310	0.036
Ag	56	5500	782	1955	——
Pb	38	2410	444	1525	0.0105
Sb			317	1440	0.0082
Bi	12.5	2030	376	950	0.0065

* Hildebrand, *loc. cit.*, pp. 181–182.

† Bieneas and Sauerwald, *Z. anorg. Chem.*, 161: 51, 1927.

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[1] J. Johnston, *J. Phys. Chem.*, 29: 882, 1925.

[2] Washburn and Read, *Proc. Nat. Acad. Sci.*, 1: 191, 1915.

[3] Dupre, *Ann. chim. Phys.*, 2: 201, 1864.

[4] Joel Hildebrand, "Solubility," Am. Chem. Soc. Monograph, p. 102, 1924.

[5] R. A. Morgen, L. G. Swenson and F. C. Nix, Tech. Pub. 43, Am. Inst. Mining and Met. Eng., 1928.

[6] R. S. Dean, *J. Am. Chem. Soc.*, 45: 1683, 1923.

[7] Endo, Sci. Repts., Tohoku Imp. Univ. 14: 503, 1925.