PHILOSOPHICAL TRANSACTIONS.

I. *On certain improvements on Photographic Processes described in a former Communication, and on the Parathermic Rays of the Solar Spectrum.* *By Sir* J. F. W. HERSCHEL, *Bart., K.H., F.R.S., &c.; in a Letter addressed to* S. HUNTER CHRISTIE *Esq., Sec. R.S.* *Communicated by* S. HUNTER CHRISTIE.

Received November 17,—Read November 17, 1842.

DEAR SIR,

231. I BEG leave herewith to submit for your inspection and that of the Royal Society, a series of photographic impressions illustrative of the chrysotype, cyanotype, and other processes, an account of which is given in the Postscript to my last paper on that subject, which has, by permission of the President and Council, been appended to the original in its printed form subsequently to the termination of the Session. In the interval which has since elapsed, besides the discovery of other photographic novelties (which may form the subject of future communications), I have been enabled materially to improve some of the processes there described; and these improvements, with a few remarks on some other points treated of in that paper, in relation to the processes in which the thermic rays are concerned, are now subjoined.

232. The positive cyanotype process described in Arts. 219, 220 of my papers, though beautiful in its effect (especially during the first few minutes of the appearance of the picture), is very precarious in its ultimate success, owing to causes there detailed. The remedies proposed are also only occasionally and partially successful, and in consequence this process, though exceedingly *easy* in its manipulations, could not be recommended as practically useful. After trying a vast variety of means to overcome these obstacles to its success, I have succeeded at last, by the simple addition of corrosive sublimate to the ammonio-citrate of iron with which the paper is prepared. The improved process, therefore, may be thus stated. Mix together equal measures of a saturated cold solution of corrosive sublimate, and a solution of am-

monio-citrate of iron, one part by weight of the salt to eleven parts water. No immediate precipitation takes place, and before any has time to do so, the mixture must be washed over paper (which should have rather a yellowish than a bluish cast), and dried. It is now ready for use, and I do not find that it is impaired by keeping. To use it, it must be exposed to the light till a faint, but yet perfectly visible picture is impressed, and till the border (if it be an engraving which is copied) has assumed a pale brown colour. Being withdrawn it is to be brushed over as rapidly as possible with a broad flat brush, dipped in a saturated solution of prussiate (ferrocyanate) of potash diluted with three times its bulk of gum-water, so strong as just to flow freely without adhesion to the lip of the vessel. All the care that is required is, that the film of liquid be very thinly, evenly, and above all, quickly spread. Being then allowed to dry in the dark, it rarely fails to produce a good picture. And what is very remarkable, it is *ipso facto* fixed as soon as dry, so at least as not to be injured by exposure to common day-light, immediately; and after a few days' keeping it becomes entirely so, and will bear strong lights uninjured. By long keeping, details at first barely seen come out, and the whole picture acquires a continually-increasing intensity, without however sacrificing distinctness; and by the same gradations its colour passes from purple to greenish-blue. Some experience, to be acquired only by practice, is necessary to determine the proper moment for withdrawing the photograph from the action of the light. If it be over-sunned, only the darker shades appear; if too little, the whole, though beautifully perfect in the first moments of its appearance, speedily runs into an indistinguishable blot.

233. The principal obstacle in the way of the employment of gold and silver as photographic ingredients for the production of negative models, to be used for re-transfers, so as to multiply positive copies, arises from the want of absolute opacity in these metals or their oxides when in a state of minute division. The same objection does not apply, or applies with much less force, to mercury, which (probably owing to its fluid state, which prevents its particles from acquiring that excessive tenuity which a laminated form would admit, by reason of their capillary forces contracting each separately deposited particle into a sphere) is one of the most opake substances (after carbon) known. I find that this high degree of blackness and opacity may be induced on a mercurial photograph prepared as in Art. 228, by a process which is in itself not a little curious and instructive, as affording a kind of parallel to the stimulating action of Mr. Talbot's second application of nitrate of silver, in his beautiful kalotype process. The nature of the process in question will be best illustrated by describing the experiment which led to it.

234. It frequently happens that papers prepared with nitrate of mercury and the ammonio-citrates or tartrates, with or without addition of tartaric or citric acid, fail to exhibit the peculiar properties described in Arts. 228, 229 at all satisfactorily. Indeed, to bring on the peculiar velvety effect there described, a high degree of intensity of sunshine seems to be an essential requisite, as, in a feeble sun, I have never

obtained even an approach to it. A paper prepared (Oct. 28, 1842) according to the instructions of Art. 229 in every respect, except in the proportion of tartaric acid (which was somewhat less than that recommended), proved very little sensitive. A strip of this paper, half shaded, acquired after a few minutes' exposure to sunshine only a feeble brown colour over the sunned portion. Being then withdrawn, it was washed over with nitrate of mercury. *Immediately* the sunned portion began to darken very rapidly while the shaded part was unaffected, and ultimately assumed a deep brown hue. Exposed while yet wet to the sunshine, this passed rapidly to intense blackness, while the portion originally shaded, which had undergone the same subsequent application, and which was now equally exposed to the sun, sustained in the short time required for bringing on this effect, no appreciable change. Indeed it seemed rather to have become more insensible than before.

235. Not alone nitrate of mercury is capable of thus exciting or stimulating the dormant photographic impression on such paper. To my very great surprise, I found the same effect to be produced by *water* sparingly applied, so as only to moisten the paper. Across the sunned and shaded portions of a strip of the mercurialized paper, exposed till a pale brown was developed in the former portion, were drawn two streaks, one of weak nitrate of mercury and one of spring water. Both, after a very short interval, passed to an intense brown on the sunned half, the shaded remaining unchanged. Edging the streak produced by the nitrate was a black border, that produced by the water was uniform. The *whole* paper was now exposed for a short time to the sun, which rapidly converted to intense blackness both the streaks on the previously sunned half, while it produced no perceptible change in the other. I found this experiment to succeed on many different varieties of paper, and with very considerable latitude in the dosage of the ingredients. It was most successful in the case of a paper prepared with a cream, formed by mixing one measure ammonio-*tartrate* of iron (strength $\frac{1}{12}$*) and two saturated protonitrate of mercury, leaving out the free tartaric acid altogether, which, among many other doses of these two ingredients, proved also, generally, the most sensitive to light.

236. Led by these indications I prepared a paper by washing, first with a weak solution of ammonio-citrate of iron (strength $\frac{1}{20}$), and when dry, with saturated protonitrate of mercury. It was exposed *when barely dry enough, not to feel damp,* with an engraving in a frame to a hazy and declining sun. In about twenty minutes a very pale and feeble photograph was produced. Excited as above, by water, it gained but little in intensity (for it deserves remark that the *increase* of apparent intensity produced by either water or the nitrate, is in direct *proportion* to the force of the original impression, which, as observed, was in this case very faint). It was then held for about five minutes in the sun (near setting), and by degrees, and with the utmost regularity of gradation over every part of the picture, each line assumed an

* By this I understand one part (by weight) salt + 11 water.

inky blackness, the lights and shades being exquisitely preserved in their due proportions, and the ground being hardly perceptibly discoloured. The result was a very beautiful and perfect negative photograph.

237. This singular power of water to excite the dormant impression, strongly recalls the analogous power of moisture to deepen the tints photographically impressed on auriferous papers, of which an instance is given in Art. 45, and of which a still more striking example is shown as follows. Let a paper be washed first with ammonio-citrate of iron, and when dry with neutralized chloride of gold, and thoroughly dried in the dark. It is then, apparently, almost insensible to light; a slip of it half exposed to sun being hardly impressed in any perceptible degree in many minutes; yet if breathed on, the impression comes out very strong and full, deepening by degrees to an extraordinary strength. Treated in the same manner, silver also exhibits a similar property*. Nor, indeed, is there any feature in photography more general or more remarkable than the influence exercised by the presence of a certain degree of moisture in favouring the action of light, whether direct or indirect.

238. There is this difference, however, in the excitement produced by simple water and by the mercurial solution, viz. that the latter is permanent, the former liable to fade; at least I have found this to be the case with the brown tinge produced by it in shade, though when blackened by a second exposure to sun no difference is perceived. On the other hand, when the nitrate is used, the brown hue frequently passes to absolute blackness without any subsequent exposure to sunshine; and in that case the photographs produced have an intensity and opacity scarcely, if at all, inferior to that of printing ink.

239. This high degree of opacity and depth, together with the comparative insensibility of the ground, is evidently capable of being most usefully applied to the production of retransfers. In fact, the photographs so produced being negative are so far fitted for the purpose, and if used as models while in this, their transition state, and as it were self-fixed, so far from being injured by the transmission of light, they are actually acquiring additional sharpness and depth by every beam which passes. By *seizing therefore the right point of dryness*, and by using a very sensitive paper to receive the impression, there is no reason to doubt of success in procuring very perfect positive transfers. Some trials I have made have satisfied me as to the practi-

* Note added Dec. 21.—The excitement is produced on such paper by the ordinary moisture of the atmosphere, and goes on slowly working its effect in the dark, apparently without *other* limit than is afforded by the supply of ingredients present. In the case of silver, it ultimately produced a perfect *silvering* of all the sunned portions. Very singular and beautiful photographs having much resemblance to Daguerreotype pictures, are thus produced; the negative character changing by keeping, and by quite insensible gradations, to positive; and the shades exhibiting a most singular *chatoyant* change of colour from ruddy-brown to black when held more or less obliquely. No doubt also gold pictures with the metallic lustre might be obtained by the same process, though I have not tried the experiment.—J. F. W. H.

cability of this, however contrary it may at first sight appear to the usual conditions of photography.

240. In the positive cyanotype process, as improved by the addition of corrosive sublimate above recommended, we are furnished with another instance of a transformation effected by heat, analogous to those described in Art. 223. A picture prepared by this process, if heated, is transformed from positive to negative and from blue to brown. On keeping the blue colour is restored, *as well as the positive character*. In Art. 224 I have referred this curious action to certain rays, which, whether they be regarded as rays of heat, or light, or of some influence, *sui generis*, accompany in the spectrum the red and orange rays, and are also copiously emitted by heated bodies short of redness. These rays are distinguished from those of light by being invisible; they are also distinguished from the purely calorific rays beyond the spectrum by their possessing the properties recorded in Arts. 160, 223, either exclusively of the calorific rays, or in a very much higher degree. They may perhaps not improperly be regarded as bearing the same relation to the calorific spectrum which the photographic rays do to the luminous one, and if the restriction to these rays of the term *thermic* as distinct from *calorific* be not (as I think in fact it is not) a sufficient distinction, I would propose the term *parathermic rays* to designate them. These are the rays (if I may indulge in speculation which I propose to bring to the test of experiment hereafter) which I conceive to be active in producing those singular molecular affections which determine the precipitation of vapours in the experiments of Messrs. Draper, Moser, and Hunt, and which will probably lead to important discoveries as to the intimate nature of those forces resident on the surfaces of bodies to which M. Dutrochet has given the name of epipolic forces. These also, I cannot help considering it as highly probable, are the rays which radiated from molecule to molecule in the interior of bodies, determine the discharge of vegetable colours at the boiling temperature (see Art. 162), and the innumerable isomeric and other atomic transformations of organic bodies which take place at temperatures below redness. The term latent light, I confess, carries with it to my mind no distinct conception; still less capable of being introduced into scientific language appears such a term as *invisible* light. Whether the rays to which such terms have been applied shall or shall not turn out, on inquiry, to be identical with my "parathermic" rays, can only be decided by experiments to be instituted for that purpose; but at all events I feel strongly disposed to insist on the distinction between *these* rays and those of *pure heat*, and in referring them to a peculiar region of the spectrum (though without denying their more sparing distribution over every other part of it), I consider them at all events as sufficiently identified by their characters, there eminently developed, to become legitimate objects of scientific discussion.

241. The action of the calorific rays, *as such*, demonstrated by the rapidity of evaporation of water or alcohol which takes place under their influence, is traced (in addition to the facts brought forward in the notes on my first paper on this subject)

in the experiments described in Arts. 205, 208, in the latter of which a chemical action, distinct from the calorific, seems also traceable. I may here also mention that the rays which operate the change of colour in muriate of cobalt from rose colour to green appear to be the calorific rays generally, and the effect to be one of simple evaporation; since under the action of the spectrum I find the green colour not restricted to the "parathermic" region, but to extend far beyond the red, and to be, in fact, commensurate with the calorific spectrum, so far as it could be traced in an experiment made under unfavourable circumstances.

I have the honour to remain, my dear Sir,

Yours very truly,

J. F. W. HERSCHEL.

Collingwood, Nov. 15, 1842.