CCIV. *On the Preparation of absolute Alcohol, and the Composition of "Proof-Spirit."* By Mr. JOSEPH DRINK-WATER. (*Communicated by Professor Graham.*)

THE following experiments were undertaken, principally, with a view to determine the relative proportions of anhydrous alcohol and water in revenue proof-spirit, for which purpose it was necessary to procure alcohol in its absolute or pure state.

The processes employed were as follows:—

Carbonate of potash was exposed to a red heat to deprive it of water, and when sufficiently cool was pulverized, and added to ordinary alcohol of specific gravity $\cdot 850$ at 60° F. till it ceased to dissolve any more; the whole was then allowed to digest twenty-four hours, being frequently agitated, when the alcohol was carefully poured off.

As much fresh-burnt quicklime as was considered sufficient when powdered to absorb the whole of the alcohol, was introduced into a retort, and the alcohol added to it; after digest-

ing forty-eight hours, it was slowly distilled in a water-bath at a temperature of about 180° F.

The alcohol thus obtained was carefully redistilled, and its specific gravity at 60° F. was found in two experiments to be $\cdot 7946$ and $\cdot 7947$; agreeing very nearly with the determination of Rudberg, which has been adopted by Gay-Lussac and others, viz. $\cdot 7947$ at 59° F.

It may be proper to state that the specific gravity was taken with a stoppered bottle, which was always counterpoised by another empty bottle of the same glass and form, placed in the opposite pan of the balance; the capacity of the weighing bottle at 60° F. was exactly $1000\cdot 01$ grains of distilled water; and it was found on trial that this bottle could be repeatedly filled with the same liquid with no greater variation than one or two hundredths of a grain.

The temperature of the room in which these experiments were made was always brought to 60° F.; and the thermometer used was a standard instrument by Newman, and extremely sensitive (being graduated to one-tenth of a degree); on being plunged into the weighing bottle filled with alcohol it displaced about $4\frac{1}{2}$ grains of that fluid; this portion was replaced from the stock quantity (brought at the time to the proper temperature) by means of a pipette.

With a view however to discover whether it were possible by means of lime to abstract any more water from the alcohol, the retort was again filled with fresh-burned and pulverized quicklime and the same alcohol mixed with it; the mixture was then allowed to digest a whole week at the ordinary temperature of the laboratory, about 60° F. After this time the alcohol was distilled off as before, but was redistilled very slowly, at first at the rate of about one drop in ten seconds (heat of water-bath 165° F.); this was continued till about one-twentieth of the whole had distilled over, the object being to allow any minute quantity of water which the alcohol might still retain to evaporate or diffuse itself into the atmosphere of absolute alcohol above it; the redistillation was then continued rapidly, the heat of the bath being increased to 180° F. till about one-twentieth more had passed over; the receiver was then changed and the remaining part slowly distilled off.

The specific gravity of this alcohol taken twice was $\cdot 7944$ at 60° F. As a further test of its purity it was divided into two equal parts; one part was again digested on quicklime, and the other on sulphate of copper deprived of water by heat, the method of operation being as follows:—

1st. Some lumps of fresh-burnt quicklime were heated to

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a red heat, and in that state quickly pulverized and introduced into the tin boiler of a small still, which was partly immersed in water to prevent the melting of the solder.

This vessel was completely filled with quicklime, and was kept corked till sufficiently cool, when the alcohol was added, but it being comparatively small in quantity the lime appeared perfectly dry; the vessel was then securely corked.

2nd. A quantity of sulphate of copper was exposed to a red heat till completely deprived of water; it was then quickly pulverized and introduced into a small tin boiler, and when cold the alcohol (which was insufficient to cover it) was added, and the vessel closely corked.

These vessels with their contents were kept at the ordinary temperature of the laboratory (about 60° F.) for four days; they were then partly immersed in a water-bath, and kept at a temperature of about 150° F. for forty-eight hours, after which the alcohol was distilled and redistilled with all the precautions before-mentioned; the temperature of the water-bath on the redistillation never exceeded 172° F., and the first tenth part was put aside in each case as possibly impure.

The specific gravities of the alcohol thus obtained were as under:—

	Alcohol distilled from desiccated sulphate of copper.	Alcohol di- stilled from quicklime.
I. . . .	·79470	·79409
II. . . .	·79472	·79412

From these experiments it would appear that sulphate of copper, when deprived of water, is not so effective as quicklime in removing the last traces of water from alcohol.

It was observed, however, that in general the specific gravity of the alcohol gradually increased, probably from its hygrometric property, by which it absorbed a minute quantity of moisture from the air on being transferred from one bottle to another; and thinking consequently that a small quantity of moisture might have been abstracted from the atmosphere during the distillation (which was conducted in the usual way), and the specific gravity thus slightly increased, I considered it desirable to make another experiment in which this source of error should be guarded against, by conducting the distillation as much as possible out of contact with the external air, and proceeded as follows.

The different portions of alcohol before obtained were mixed together, when the specific gravity was found to be ·7947; this alcohol was again digested at a temperature of about 150° F. for fourteen days with quicklime, previously

heated to redness, as in the former experiment; it was then slowly distilled out of contact with the external atmosphere by means of a tube which passed from the condenser through a cork into the bottle in which it was to remain (the temperature of the water-bath was 175° F.), and the first tenth part was put aside as possibly containing a minute quantity of water; the remainder was then distilled off at 178° to 180° F.

This alcohol was quickly transferred to a dry retort and redistilled in a similar way (heat of water-bath 172° F.); the first tenth part was put aside, and the remainder kept as being pure anhydrous alcohol, or as free from water as it is possible to obtain it by this process. The specific gravity was taken the next day with all the precautions before mentioned, the alcohol being also kept during the time of transference as much as possible out of contact with humid air, when the results of four trials were as follow :—

Temperature of room 60° F. Barometer 29·810.

I.	·793836
II.	·793806
III.	·793798
IV.	·793804
Mean	·793811

A portion of this alcohol was subsequently digested with quicklime for three months, it was then distilled, and its specific gravity was found to be exactly the same as before.

We may therefore conclude with considerable certainty that the number ·79381 expresses the specific gravity of absolute alcohol at 60° F., within a very close degree of approximation.

My attention was next directed to the best method of determining the relative proportions of absolute alcohol and water which exist in legal or revenue proof-spirit.

There is some ambiguity in the wording of the act of parliament 58 Geo. III. c. 28, which defines proof-spirit to be “such as shall at the temperature of fifty-one degrees by Fahrenheit’s thermometer weigh exactly twelve-thirteenth parts of an equal measure of distilled water,” but the temperature of the water is not stated: there is no doubt however that the temperature of 51° F. was intended to apply to the water as well as to the spirit; therefore taking water at 51° F. as unity, the specific gravity of proof-spirit at that temperature will be ·92308; or raising the temperature of both to 60° F., the specific gravity will be ·91984—the expansions being calculated from Gilpin’s Tables*.

* Philosophical Transactions for 1794.

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It was found by a few preliminary experiments that the specific gravity .91984 would lie between a mixture of 49 absolute alcohol + 51 water, and a mixture of $49\frac{1}{2}$ absolute alcohol + $50\frac{1}{2}$ water, all by weight. Mixtures were therefore made in these proportions in an apparatus procured for the purpose, consisting of two light flasks each capable of containing about 2200 grains of water. The alcohol and water were weighed separately in these flasks with the greatest care; after which the flasks were joined without mixing the liquids, the neck of one being ground into the neck of the other for that purpose; the liquids were then thoroughly mixed by transferring them alternately from one flask to the other. The flasks were disconnected when the mixed contents became cool, which were then transferred to a clean and dry well-stoppered bottle, and further secured by tying a piece of caoutchouc over the stopper.

It may also be proper to mention, that when placed in the balance, these flasks were always counterpoised by other empty flasks of the same material, and of very nearly equal size and shape; and to prevent loss from evaporation, a ground glass cap was placed over the mouth of each flask as soon as the exact weight was obtained. The errors of observation could not, I believe, in any case exceed one-hundredth of a grain, as the balance used in these experiments was one of Robinson's best instruments, which was previously adjusted by Newman expressly for the purpose; it was turned with its greatest load by less than one-hundredth of a grain.

The proportions of absolute alcohol and water mixed were as under, all by weight. Temperature of room 60° F. Barometer 29.832.

First mixture.—588 grs. alcohol + 612 grs. water, being in the proportion of 49 grs. alcohol + 51 grs. water.

Second mixture.—594 grs. alcohol + 606 grs. water, being in the proportion of $49\frac{1}{2}$ grs. alcohol + $50\frac{1}{2}$ grs. water.

After twenty-four hours, the bottles having been frequently shaken, the specific gravities of both mixtures were taken, with all the precautions detailed in the experiments on absolute alcohol: and in order to observe if the full condensation was gradual and required time for its completion, the mixtures were allowed to stand, with occasional agitation, for a further period of twenty-four hours, when the liquids were again weighed. The results were as follows:—

At 24 hours, temperature of room 60° F., barometer 29.630.
At 48 hours, temperature of room 60° F., barometer 29.550.

*First Mixture.**Second Mixture.*

I. .920361	} after standing 24 hours.	I. .919297	} after standing 24 hours.
II. .920358		II. .919297	
III. .920361	} after standing 48 hours.	III. .919307	} after standing 48 hours.
Mean .920360		Mean .919300	

It thus appears that both liquids attained a fixed specific gravity within the first twenty-four hours.

If we now express the preceding results by measure, and make the proportion of alcohol a constant quantity in the two mixtures, we have—

Alcohol and water by weight.		Alcohol and water by measure.		Spec. gravity of the mixtures.
Alcohol.	Water.	Alcohol.	Water.	
49 + 51	} in the pro- portion of	100 + 82	62105	.92036
49½ + 50½		100 + 80	98470	.91930
Difference . .		163635		<u>106</u>

Dividing the difference of the quantities of water by the difference of specific gravity, we get .015437, the mean quantity of water corresponding to each unit of difference in the specific gravities. But the difference between the specific gravity of proof-spirit and .91930, one of the observed specific gravities, is 54; therefore we have $54 \times .015437 = .8336$, the quantity of water to be added to the spirit of that specific gravity to form proof-spirit, as follows:—

	Alcohol.	Water.	Specific gravity.
	100	+ 80	.9847
Add water	100	+ .8336	54
Proof-spirit =	100	+ 81.8183	.91984

From the foregoing data the following results have been calculated:—

Composition of Proof-Spirit.

Alcohol and water.		Specific gravity at 60° F.	Bulk of mixture of 100 measures of alcohol + 81.82 water.	Strength per cent. above proof of absolute alcohol.
By weight.	By measure.			
Alcohol. Water. 100 + 103.09 or in 100 49.24 + 50.76	Alcohol. Water. 100 + 81.82	.91984	175.25	75.25

It is remarkable that Dr. A. Steel * arrived at almost the

* Dr. Steel's papers, which contain much valuable information on the specific gravity of spirits, are contained in the 'Records of General Science,' vol. i. pp. 222-255.

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same composition for proof-spirit, namely, 49·2 and 50·8, partly by experiment and partly by calculation.

The table of M. Lowitz, showing the quantity of alcohol in spirits of different specific gravities (which is to be found in most chemical works published in this country), also agrees with these experiments at this particular point, although from some experiments which I have had occasion to make, I have found that at other points this table is incorrect; and as it is frequently consulted by chemists, it was considered desirable to make a few mixtures of pure alcohol and water, from which to calculate a more correct table for estimating the quantity of alcohol in mixtures containing not more than 10 per cent. of that liquid.

Eleven mixtures were therefore made, containing exactly $\frac{1}{2}$, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 per cent. by weight of absolute alcohol. These mixtures were made in the same apparatus, and with all the precautions described in the former experiments. They were allowed to stand at least 24 hours with occasional agitation before the specific gravities were taken, and several of them were again taken after a period of 48 and 72 hours, without any sensible variation.

The particulars are set forth in the following table:—

No. of mixtures.	When the mixtures were made.				When the specific gravities were taken.			
	Alcohol and water mixed.		Quantity of alcohol per cent. by weight.	Temperature of room.	Height of barometer.	Specific gravity of mixture at 60° F.	Temperature of room.	Height of barometer.
	Alcohol.	Water.						
1.	grs. 5·5 +	grs. 1094·5	0·5° F.	60	29·700	·99905	60° F.	29·690
2.	11·0 +	1089·0	1·0	60	29·700	·99813	60	29·690
3.	22·0 +	1078·0	2·0	60	29·690	·99629	60	29·500
4.	33·0 +	1067·0	3·0	60	29·718	·99454	60	29·610
5.	44·0 +	1056·0	4·0	60	29·690	·99283	60	29·500
6.	55·0 +	1045·0	5·0	60	29·718	·99121	60	29·610
7.	66·0 +	1034·0	6·0	60	29·742	·98963	60	29·644
8.	77·0 +	1023·0	7·0	60	29·742	·98813	60	29·644
9.	88·0 +	1012·0	8·0	60	29·670	·98668	60	29·800
10.	99·0 +	1001·0	9·0	60	29·670	·98527	60	29·800
11.	110·0 +	990·0	10·0	60	29·800	·98389	60	29·566

From the above data the following table has been calculated:—

Table of the quantity of absolute Alcohol by weight contained in mixtures of Alcohol and Water of the following specific gravities :—

Specific gravity at 60° F.	Alcohol, per cent. by weight.	Specific gravity at 60° F.	Alcohol, per cent. by weight.	Specific gravity at 60° F.	Alcohol, per cent. by weight.	Specific gravity at 60° F.	Alcohol, per cent. by weight.	Specific gravity at 60° F.	Alcohol, per cent. by weight.
1.0000	0.00	.9967	1.78	.9934	3.67	.9901	5.70	.9869	7.85
.9999	0.05	.9966	1.83	.9933	3.73	.9900	5.77	.9868	7.92
.9998	0.11	.9965	1.89	.9932	3.78	.9899	5.83	.9867	7.99
.9997	0.16	.9964	1.94	.9931	3.84	.9898	5.89	.9866	8.06
.9996	0.21	.9963	1.99	.9930	3.90	.9897	5.96	.9865	8.13
.9995	0.26	.9962	2.05	.9929	3.96	.9896	6.02	.9864	8.20
.9994	0.32	.9961	2.11	.9928	4.02	.9895	6.09	.9863	8.27
.9993	0.37	.9960	2.17	.9927	4.08	.9894	6.15	.9862	8.34
.9992	0.42	.9959	2.22	.9926	4.14	.9893	6.22	.9861	8.41
.9991	0.47	.9958	2.28	.9925	4.20	.9892	6.29	.9860	8.48
.9990	0.53	.9957	2.34	.9924	4.27	.9891	6.35	.9859	8.55
.9989	0.58	.9956	2.39	.9923	4.33	.9890	6.42	.9858	8.62
.9988	0.64	.9955	2.45	.9922	4.39	.9889	6.49	.9857	8.70
.9987	0.69	.9954	2.51	.9921	4.45	.9888	6.55	.9856	8.77
.9986	0.74	.9953	2.57	.9920	4.51	.9887	6.62	.9855	8.84
.9985	0.80	.9952	2.62	.9919	4.57	.9886	6.69	.9854	8.91
.9984	0.85	.9951	2.68	.9918	4.64	.9885	6.75	.9853	8.98
.9983	0.91	.9950	2.74	.9917	4.70	.9884	6.82	.9852	9.05
.9982	0.96	.9949	2.79	.9916	4.76	.9883	6.89	.9851	9.12
.9981	1.02	.9948	2.85	.9915	4.82	.9882	6.95	.9850	9.20
.9980	1.07	.9947	2.91	.9914	4.88	.9881	7.02	.9849	9.27
.9979	1.12	.9946	2.97	.9913	4.94	.9880	7.09	.9848	9.34
.9978	1.18	.9945	3.02	.9912	5.01	.9879	7.16	.9847	9.41
.9977	1.23	.9944	3.08	.9911	5.07	.9878	7.23	.9846	9.49
.9976	1.29	.9943	3.14	.9910	5.13	.9877	7.30	.9845	9.56
.9975	1.34	.9942	3.20	.9909	5.20	.9876	7.37	.9844	9.63
.9974	1.40	.9941	3.26	.9908	5.26	.9875	7.43	.9843	9.70
.9973	1.45	.9940	3.32	.9907	5.32	.9874	7.50	.9842	9.78
.9972	1.51	.9939	3.37	.9906	5.39	.9873	7.57	.9841	9.85
.9971	1.56	.9938	3.43	.9905	5.45	.9872	7.64	.9840	9.92
.9970	1.61	.9937	3.49	.9904	5.51	.9871	7.71	.9839	9.99
.9969	1.67	.9936	3.55	.9903	5.58	.9870	7.78	.9838	10.07
.9968	1.73	.9935	3.61	.9902	5.64				