the presence of a blood red color in the latter as against a brown color in the former. The results recorded in Table VI show that the volume of mercuric chloride solution required to bleach the red color to the point when no further considerable change takes place on adding 0.3 cc., is roughly proportional to the quantity of thiocyanate present. This reaction therefore furnishes a basis for an approximate estimation of thiocyanates.

TABLE VI.

No.	Mg. SCN.	Cc. HgCl₂ solution used.
1	5	0.6
2	50	5.4
3	100	9.9
4	250	18.6

Significance of the Results.—It has been stated by Kern[1] and confirmed by us that in the presence of thiocyanates, palladium chloride may fail to give a reliable indication of the presence of iodides and that palladium nitrate may fail to give a reliable separation of iodides from chlorides and bromides. The need for a test for thiocyanates in the presence of iodides is therefore evident. Moreover, it is hardly necessary to state that in the presence of alkali halides only, the entire preliminary procedure may be dispensed with in testing for thiocyanates. To the solution, acid with dilute nitric acid, it is only necessary to add silver nitrate, and after filtering to treat the precipitate with sodium chloride solution.

Summary.

1. The sensitiveness of the ferric thiocyanate test for thiocyanates has been determined.

2. Data are supplied showing the extent of the interference of iodides, acetates and nitrites.

3. A procedure has been devised for the systematic detection of thiocyanates depending upon the ability of a 5% sodium chloride solution to transpose silver thiocyanate.

4. Numerous tests analyses show the reliability of the method.

FREE ENERGY AND HEAT CAPACITY.

By James M. Bell.

In a recent paper, T. W. Richards[2] writes as follows:

"I was able to show, in cases of certain typical reversible galvanic cells, that when free energy change increases with rising temperature, total energy change decreases, and *vice versa.*"

And appended to this is a footnote as follows:

[1] *Chem. News*, **32**, 242 (1875).

[2] This Journal, **36**, 2433 (1914).

"That is to say, expressed mathematically $dA/dT = -n.dU/dT$, in which A represents free energy, U total energy and n a number, which was often found to be about 2. Of course dU/dT is nothing more or less than the change of heat capacity during the reaction. J. M. Bell has questioned the sufficiency of the evidence, but he has neglected to note that although Marignac's data (upon which I relied) were perhaps absolutely not very accurate, they are relatively one to another much more to be depended upon; and in this question relative accuracy alone is concerned. *J. Phys. Chem.*, **9**, 402 (1906)."

In the paper[1] referred to by Richards, I showed that the possible errors, whose magnitude Marignac[2] was careful to state, were in some cases so great as to leave an uncertainty in the quantity sought (dU/dT) greater than the quantity itself. That there were large errors seems to be admitted by Richards, who, however, now makes the claim that Marignac's data were relatively to one another much more to be depended upon. In reply to this, there are here offered two statements of fact which refute the claim.

(1) Marignac makes no such claim about his own data, for in comparing results[3] by taking differences (exactly as Richards does) he frankly admits a possible error of two units in the third decimal place *for each solution,* or a possible error of four units in the third decimal place for the differences. If the numbers were relatively accurate, the error should cancel out. Where the signs of the errors are unknown, the possible error in the final result must be considered as the accumulation of all the possible errors. Marignac clearly recognized this point.[4]

(2) In determining the heat capacity of a solution of the composition $CuSO_4.200H_2O$, Richards takes the mean of two values given by Marignac:[5] 0.9503 between 18° and 23°, and 0.9528 between 22° and 53°. The very fact that the mean was taken indicates that they were considered as duplicates. They differ by more than two units in the third place of decimals; whereas, in my paper I showed that with an error of one unit in the third place of decimals, there was an uncertainty in the quantity to be determined greater than the quantity itself. The wide difference between numbers considered by Richards as duplicates at once refutes his claim of greater relative accuracy, for this relative accuracy could not be greater than the degree of duplication of results.

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[1] This reference should be *J. Physic. Chem.*, **9**, 381 (1905).

[2] *Ann. chim. phys.*, [5] **8**, 415 (1876).

[3] *Loc. cit.*, p. 421.

[4] On page 415 of his paper (*loc. cit.*) Marignac says of individual results: ". . . . . la troisième (décimale) peut être déjà affectée d'une erreur de 1 ou 2, rarement de 3 unités." And on page 421 of the same paper he says of differences: ". . . . . la limité des erreurs d'observation celles-ci pouvant bien s'élever, entre les deux expériences à $^{30}/_{10000}$ ou $^{40}/_{10000}$."

[5] *Loc. cit.*, p. 418.

A Reply to the Foregoing Communication.

Of course I heartily agree with Professor Bell in regard to the general proposition suggested by the foregoing note. There is great need of caution that the limits of accuracy of the data should not be overstepped in any conclusion drawn from them. My footnote, to which he takes exception, is not happily expressed. It was, moreover, too brief to express the exact state of the case. Accordingly, I beg leave to withdraw the wording of the four lines concerning Dr. Bell, with apologies to him, and to substitute for these four lines the following more complete and accurate statement:

"Dr. J. M. Bell has questioned the sufficiency of the evidence. It must be admitted that Marignac's data, upon which I depended, leave something to be desired; but, nevertheless, a careful comparison of the figures seems to show that large errors were comparatively rare.[1] This being the case, it seems to me that although such a single comparison among these data as that adduced by Dr. Bell might be subject to an important chance of mistake, nevertheless, when a number of results (with a range as wide as those employed in my reasoning) combine in pointing toward any given verdict, the chances are much in favor of the correctness of the verdict. Marignac's own use of his data justifies this opinion."

A few quotations from Marignac's remarks, following his tables of results, may make this point clear.

"Mais on peut espérer que les erreurs d'expériences se compensant en grande partie sur un aussi grand nombre de déterminations, les conséquences tirées de leur ensemble seront suffisamment justifiées. . . . .

"Mais à côté de ces observations générales, ces expériences prouvent que l'accroissement de la chaleur spécifique est très rapide pour certaines solutions. Ce fait est surtout remarquable pour le sulfate de cuivre, et il m'est impossible de l'attribuer à une erreur, car j'ai fait trois fois, à trois époques différentes, la série entière des déterminations relatives à ce sel, dans les deux conditions de température et je suis toujours retombé sensiblement sur les mêmes nombres dont j'ai indiqué la moyenne. . . . . . .

"Il est impossible de méconnaître un certain degré de parallélisme dans les diverses séries de sels. Les bases se rangeraient le plus souvent à peu pres dans le même ordre. . . . .

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[1] Full discussion of this comparison of Marignac's figures would require too much space for the present note. On tabulating his results at different temperatures for the most dilute solutions containing bivalent metals (which alone came into consideration), it appears that an error of even as much as 1 in the third decimal place was probably not frequent. The mean deviation from the average in all these cases (except that of copper sulfate, which received special discussion) is only 0.0003, and one might well conclude that most of the individual values are probably within 0.05% of the truth. Marignac's cautious temperament apparently led him to claim less than he was entitled to claim.

"La différence entre les chaleurs moléculaires du sulfate et du chlorure de potassium est exactment la même que celle qu'on observe entre le sulfate et le chlorure de sodium........

"Il y a identité presque absolue de chaleur moléculaire pour les solutions de sulfate et de chromate de potasse, et de même pour celles d'acide sulfurique et d'acide chromique."......etc.[1]

These quotations show that Marignac, while fully recognizing the possibility of occasional wide deviations, had considerable confidence in his final results, and thought them worthy of employment in parallel comparisons involving a number of data. I used Marignac's values (the best data available) for a kind of comparison not unlike that described in the above quotations, and in a spirit essentially in accord with his. I cannot help thinking that they still deserve this degree of confidence. It should be noted, also, that the special case cited by Dr. Bell is one of the very least significant of all those which I used. If all the cases had been so little decisive as this one, I should agree with Dr. Bell, and should never have drawn the conclusion in question. This is a case of statistical reasoning, which depends not upon a few cases, but rather upon the consensus of all.

Further discussion of the matter may well be postponed until Marignac's figures have been verified or disproved by new experimental determinations, already begun.

<div align="right">THEODORE W. RICHARDS.</div>

THE INFLUENCE OF PRESSURE ON SOLUBILITY.

By HERBERT F. SILL.

Introduction.

Experimental values for the terms involved in the equation $T \, dA/dT = Q$ have been applied with good agreement for the processes of fusion and of vaporization in one-component systems. The same is true for vaporization of mixtures (isothermal distillation).

For the important case of change of state in two-component solid-liquid systems (solution and precipitation) complete experimental data have heretofore been lacking.

When both the influence of pressure and of temperature on the solubility of a substance are known, as well as the volume change involved, the relationship dA/dT is obtainable as the product $ds/dT \; dp/ds \; (V_2 - V_1)$. The significance of these terms may be stated as follows:

Let a large amount of saturated solution at the temperature T be in contact with the solute at the pressure p. Then dp represents the increase in pressure necessary to cause one gram more of the solute to pass into

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[1] Oeuvres Complet, II, 630, 632. *Ann. chim. phys.*, [5] 8, 421–425 (1876).