

Chemistry. — “The fictitious heats of solution of enantiotropic modifications at their transition point”. By Prof. ERNST COHEN and Mr. H. L. BREDÉE.

(Communicated at the meeting of April 25, 1925).

Introduction.

1. In his “Recherches expérimentales et théoriques sur les Equilibres Chimiques”¹⁾ LE CHATELIER, a long time ago, has pointed at a highly interesting relation which must exist at the transition point of enantiotropic modifications. If we call these two modifications, which are in equilibrium with each other at the temperature of transition T_0 , α and β , the temperature coefficients of the solubility at T_0 $\left(\frac{dc}{dT}\right)_\alpha$ and $\left(\frac{dc}{dT}\right)_\beta$, respectively, the fictitious heats of solution Q_α and Q_β , then, according to LE CHATELIER we have at T_0 :

$$\frac{\left(\frac{dc}{dT}\right)_\alpha}{\left(\frac{dc}{dT}\right)_\beta} = \frac{Q_\alpha}{Q_\beta} \dots \dots \dots (1)$$

About this point LE CHATELIER observes: “Il serait intéressant de vérifier cette conséquence de la formule, qu’au point de transformation le rapport des tangentes est égal au rapport des chaleurs de dissolution:

$$\frac{\frac{dc}{dT}}{\frac{dc'}{dT}} = \frac{L}{L'}$$

Only recently P. MONDAIN MONVAL²⁾ has taken up the testing of this “Law of Tangents”, choosing for his object those modifications of ammonium nitrate (the β -rhombic and the α -rhombic, which we shall indicate by the names of modification III and IV) which have their transition point³⁾ at 32°.3 C. From his experiments he deduces:

$$\frac{Q_\alpha}{Q_\beta} = 1.158; \quad \frac{\left(\frac{dc}{dT}\right)_\alpha}{\left(\frac{dc}{dT}\right)_\beta} = 1.17.$$

¹⁾ Paris 1888; pag. 165.

²⁾ C. R. Paris 177, 175 (1923); Thèses, Paris 1924; Ann. de Chimie 3, 72, 121 (1925).

³⁾ ERNST COHEN and J. KOOY, These Proceedings 27, 65 (1924); also Zeitschr. f. physik. Chemie 109, 81 (1924).

Here he observes: „Si nous rapprochons les valeurs de ces rapports nous voyons que l'écart qui existe entre elles est d'environ 1 0/0. Cet accord excellent tient évidemment en partie à une heureuse coïncidence. En égard à la difficulté des mesures et à la précision respective avec laquelle elles ont été effectuées, un écart de 4 à 5 0/0 n'aurait rien que d'acceptable”, and his final conclusion is: „Les mesures que nous avons effectuées sur les modifications allotropiques du nitrate d'ammonium aux environs de 32° vérifient donc plus exactement qu'on ne pouvait l'espérer la loi du rapport des tangentes”.

2. We cannot agree with this opinion. For, the agreement which MONDAIN MONVAL assumes from his measurements, does not really exist. It seems to exist, because he chooses quite arbitrary values out of his experimental data. Here again we have a case as is so often found in the literature, when we have to test thermodynamic relations. MOESVELD ¹⁾ has already directed attention to this fact, and we wish to point out here, that it is of great importance to trace the cause of this non agreement, when it seems that there is a discrepancy between theory and experiment, as such an investigation often leads to the discovery of new phenomena. For instance, during our investigations on the metastability of matter ²⁾, new phenomena have been brought to light, and these could be studied quantitatively, because we chose for our starting-point the divergencies between calculation and experiment which had appeared, when the equation of CLAPEYRON-CLAUSIUS was applied to the modifications III and IV of ammonium nitrate.

3. While, in an investigation by COHEN and HELDERMAN ³⁾, the curves of the intermediate heats of solution of the two forms of ammonium nitrate mentioned, had been accurately determined, we have very carefully measured the values of $\left(\frac{dc}{dT}\right)_\alpha$ and $\left(\frac{dc}{dT}\right)_\beta$ at the transition temperature (32° 3 C.) in order to test the relation of LE CHATELIER. In the present paper we describe the investigation referring to it, and in conjunction with it, a discussion of the results of MONDAIN MONVAL.

A. *The Materials used.*

4. The ammonium nitrate which we used in our investigation was obtained by recrystallizing an already pure commercial preparation several times out of carefully distilled water. An analysis, to show the degree of purity finally attained was made, according to the method, described

¹⁾ The Testing of BRAUN's Law, Utrecht 1918, page 7.

²⁾ These Proceedings 27, 65; 28, 1 (1924); Zeitschr. f. physik. Chemie 109, 81; 113, 145 (1924).

³⁾ These Proceedings 28, 2 (1924); Zeitschr. f. physik. Chemie 113, 145 (1924).

in KRAUCH "Die Prüfung der Chemischen Reagentien auf Reinheit" ¹⁾). No impurities were found.

5. We have also ascertained the purity of our material by determining the solubility of crystals prepared by successive crystallizations, according to the method described hereafter. In this way a certain crystallization gave at 20°.00 the values of 65.24 and 65.24. Crystals of the next crystallization gave the values of 65.25; 65.24 and 65.26.

B. The solubility determinations.

1. General observations.

6. The greatly divergent values which are found in the literature for the solubility of ammonium nitrate at one and the same temperature ²⁾, prove already that it is very difficult to carry out reliable determinations for this highly soluble salt. For this reason we have taken very great pains with these measurements, and have succeeded in carrying out the determinations with an accuracy of 0.02 to 0.03 %₀, in which equilibrium was always reached, starting from unsaturated as well as supersaturated solutions. Great accuracy is required, as, when LE CHATELIER's equation is to be tested, it is just the point to fix the differential quotients, which from their very nature are very susceptible to slight errors in the values of solubility. All the determinations were carried out in triplicate, while the weighings (on a BUNGE balance, which allowed an accuracy of the weighings to 0.1 mgr.) were reduced to vacuum. Our weights were calibrated according to the well known method of F. KOHLRAUSCH. The thermometers used were compared with an instrument graduated in tenths of a degree, and calibrated by the Physikalisch-Technische Reichsanstalt at Charlottenburg, the zero point of which we have controlled. In our thermostats, in which the equilibrium of solution was attained by shaking water with excess of salt, was always a BECKMANN thermometer, divided into hundredths of a degree. The regulation of the temperature was brought about by a regulator according to OSTWALD (capacity of the bulb about 500 cc), which we filled with tetrachlorethane, a liquid which has the advantage over toluene in being non-inflammable, which is very convenient when filling the bulb. The time of shaking varied between 4 and 48 hours. The temperature variations of the thermostat during a short period were not greater than 0.01 degree, at 5° and 10° two hundredths of a degree at most. The shaking of the solutions in the thermostat was done by means of the acetène-apparatus, which has been described by COHEN and BRUINS in a former paper ³⁾.

¹⁾ Berlin, 1896. Dritte Auflage, S. 32.

²⁾ A synopsis is found in MONDAIN MONVAL. See note 2 page 377.

³⁾ Zeitschr. f. physik. Chemie **93**, 43 (1918).

7. In the analysis of the saturated solutions, which, also at the higher temperatures, had to be carried out without loss of liquid (owing to evaporation) the method was followed which had been indicated by COHEN and MOESVELD ¹⁾: the curve was determined which represents the specific volume of aqueous solutions of ammonium nitrate as function of the concentration (at a definite temperature). The concentration of the saturated solutions is then found by determining their specific volume (at the temperature for which the curve mentioned has been fixed) and by calculating the concentration from the equation which represents the relation between specific volume and concentration.

8. As the temperature coefficient of the solubility of ammonium nitrate is very great, the pycnometer, into which the saturated solution is pressed, must, during this manipulation, be totally immersed in the thermostat in which equilibrium of solution is reached. For particulars of this technique we refer to the paper by ERNST COHEN, WILHELMA A. T. DE MEESTER and A. L. TH. MOESVELD ²⁾ on the influence of pressure on the solubility of substances V, especially par. 11.

2. *The determination of the solubility of Ammonium nitrate IV.*

9. The range of stability of modification IV lies ³⁾ between -16° and $+32^{\circ}.3$ C.

Our determinations of solubility have been carried out at $0^{\circ}.00$; $5^{\circ}.00$; $10^{\circ}.00$; $15^{\circ}.00$; $20^{\circ}.00$; $25^{\circ}.00$; $30^{\circ}.00$ and $32^{\circ}.00$ C.

In order to determine the concentration of saturated solutions between 0° and $32^{\circ}.3$ C. we might actually have used the equation previously found by COHEN, HELDERMAN and MOESVELD ⁴⁾, which represents the relation between specific volume and concentration of solutions of ammonium nitrate at $32^{\circ}.3$ C.:

$$(\nu_c)_{32^{\circ}.3} = 1.00507 - 0.00392087c + 0.0000051003c^2 - 0.00000000566c^3. \quad (2)$$

Meanwhile we have again determined this relation.

10. For this purpose we prepared solutions of accurately known concentration by weighing (in flasks, similar to those which were used for the determinations of solubility) salt (which had been strongly dried under particular precautions which have previously been described ⁵⁾) and water

¹⁾ Zeitschr. f. physik. Chemie **94**, 482 (1920).

²⁾ These Proceedings **28**, 108 (1924); also Zeitschr. f. physik. Chemie **114**, 321 (1924).

³⁾ ERNST COHEN and J. KOOY, These Proceedings **27**, 65 (1924); also Zeitschr. f. physik. Chemie **109**, 81 (1924).

⁴⁾ See these Proceedings **27**, 565 (1924), especially par. 9. Also Zeitschr. f. physik. Chemie **112**, 135 (1924), especially par. 9.

⁵⁾ See these Proceedings **27**, 565 (1924). Also Zeitschr. f. physik. Chemie **112**, 135 (1924), especially par. 9.

the specific volume of these solutions was then determined at 32°3 C. in the way described in par. 8. Great care was taken that no evaporation could take place during the solving of the salt, which was brought about by heating: the flasks were closed during the heating.

The results thus obtained are given in table 1.

TABLE 1.
Temperature 32°3 C.

Concentration in gr. per 100 gr. of solution	Spec. vol. found C. and B.	Spec. vol. calculated C. and B. equation (3)	Spec. vol. calculated C. H. and M. equation (2)
25.00	0.91012	0.91011	0.91015
34.99	0.87377	0.87375	0.87387
44.98	0.83829	0.83830	0.83850
54.98	0.80374	0.80372	0.80398
64.98	0.77003	0.77002	0.77028
70.65	0.75125	0.75129	0.75152

According to the method of least squares we find from the values in the first and second columns:

$$(v_c)_{32^{\circ}3} = 1.00529 - 0.00392915c + 0.0000049640c^2 - 0.00000000333c^3. \quad (3)$$

From the second and third columns of table 1 we see that this equation describes the observations. Further we observe that the differences in concentration which the equations (2) and (3) yield for a given specific volume, attain at most an amount of 0.08 per cent.

11. The results of the solubility determinations of modification IV are summarized in table 2. By means of the method of least squares we find from it for $c_{IV} = f(t)$:

$$c_{IV} = 54.241 + 0.6106t - 0.00297t^2 \quad . \quad . \quad . \quad (4)$$

Columns 6, 7 and 8 of table 2 prove that this equation holds good.

3. The determination of the solubility of Ammonium nitrate III.

12. The range of stability of this modification (III) lies between 32°3 and 84°2 C. Our solubility determinations within this range have been made at 33°00; 36°00; 39°00; 42°00; 45°00 and 48°00 C.

The curve which represents the specific volumes of solutions of ammonium nitrate as function of the concentration, has been fixed for

TABLE 2.
Solubility of Ammonium nitrate, Modification IV, in water.

Temp.	Period of shaking in hours	v_c found	v_c mean	Solubility; gr. of salt per 100 gr. of solution			$C_{\text{calc.}} - C_{\text{found}}$
				found from v_c	mean found	calculated	
0°.00	5½	0.80630	0.80629	54.23	54.23	54.24	+ 0.01
	4½	0.80627 *)		54.24			
	4½	0.80630 *)		54.23			
5°.00	4	0.79605 *)	0.79605	57.23	57.23	57.22	- 0.01
	5	0.79608		57.22			
	5	0.79603		57.24			
10°.00	4½	0.78656 *)	0.78651	60.04	60.05	60.05	± 0.00
	5	0.78650		60.06			
	5½	0.78646		60.07			
15°.00	4½	0.77740 *)	0.77741	62.77	62.76	62.73	- 0.03
	5½	0.77738		62.77			
	5½	0.77745		62.75			
20°.00	4	0.76917 *)	0.76914	65.24	65.24	65.27	+ 0.03
	4	0.76916 *)		65.24			
	24	0.76910		65.26			
	4	0.76912 *)		65.25			
	48	0.76914		65.24			
25°.00	24	0.76123	0.76122	67.63	67.63	67.65	+ 0.02
	24	0.76118		67.64			
	5	0.76125 *)		67.62			
30°.00	24	0.75375	0.75374	69.90	69.90	69.89	- 0.01
	24	0.75377		69.89			
	5	0.75370 *)		69.91			
32°.00	24	0.75087	0.75090	70.78	70.77	70.74	- 0.03
	24	0.75090		70.77			
	24	0.75092		70.76			

*) signifies: starting from supersaturated solution.

50°.00 C. so that the saturated solutions which were formed at the highest temperature investigated (48°) could never crystallize during the determination of their specific volume.

The equation of the curve $(v_c)_{50.00} = f(c)$ was obtained by determining the specific volume at 50° of solutions which contained 15, 25, 35, 45, 55, and 75 % of salt respectively (sum = 100), and which had been prepared by weighing, as is described in par. 10. Table 3 contains the results of the determinations of the specific volume.

TABLE 3.
Specific Volume of Ammonium nitrate solutions of different concentrations.
Temp. 50°.00 C.

Weight of salt in grms	Weight of solution in grms	Concentration grms of salt in 100 gr. of sol.	v_c found	v_c mean found	v_c calc.	v_c calc.-found $\times 10^5$
5.1247	34.1904	14.99	0.95527	0.95525	0.95532	+ 7
5.1247	34.1904	14.99	0.95522			
10.8391	43.3554	25.00	0.91826	0.91828	0.91822	- 6
10.8391	43.3554	25.00	0.91830			
15.1917	43.4148	34.99	0.88206	0.88207	0.88192	- 15
15.1917	43.4148	34.99	0.88208			
19.9609	44.3810	44.98	0.84626	0.84630	0.84631	+ 1
19.9609	44.3810	44.98	0.84634			
24.9593	45.3964	54.98	0.81123	0.81122	0.81136	+ 14
24.9593	45.3964	54.98	0.81120			
28.4039	43.7149	64.98	0.77708	0.77710	0.77708	- 2
28.4039	43.7149	64.98	0.77712			
32.1572	42.8859	74.99	0.74346	0.74348	0.74341	- 7
32.1572	42.8859	74.99	0.74350			

By means of the method of least squares we find:

$$(v_c)_{50.00} = 1.01227 - 0.0038565c + 0.000003855c^2 - 0.0000000319c^3. \quad (5)$$

From columns 5, 6 and 7 of table 3 we see that the equation describes the experimental data.

13. We have also controlled the equations (3) and (5) mutually, by determining the specific volume of the solution, saturated at 32°.3, at that temperature as well as at 50°.00 C, and by deducing from it the concentration of the solution by means of the equations (3) and (5).

In this way we found from the determinations of the specific volume at 32°.3 C. the values 70.87

and 70.88

and from the determinations of the spec. vol. at 50°.00 C. the values 70.87
and 70.86,

in other words: complete agreement.

14. As regards the determinations of solubility of modification III itself may be observed that they were done in the very same way as those of modification IV. The results are found in table 4. By means of the method of least squares we find for $c_{III} = f(t)$:

$$c_{III} = 57.861 + 0.4384 t - 0.00111 t^2 \quad (6)$$

From columns 6, 7 and 8 of table 4 we see that this equation describes the observations.

C. Calculation of the Transition temperature.

15. The point of intersection of the curves, represented by the equations (4) and (6) gives for the transition temperature

$$t = 32°.27 \text{ C.}$$

while $c_{IV} = c_{III} = 70.85$.

So there is complete agreement between this result and the fact that COHEN and KOOY¹⁾ have found the temperature of transition IV \rightleftharpoons III at 32°.3 C. We wish, however, to observe that too great a value must not be attached to this agreement, as for $t = 31°.8$ or $32°.8$ the two equations give a difference in the solubility of only 0.025 per cent, a difference which lies within the errors of the measurements.

D. Calculation of $\left(\frac{dc}{dT}\right)_{IV}$ and $\left(\frac{dc}{dT}\right)_{III}$ at the Transition temperature.

16. If we call the values

$$\left(\frac{dc}{dT}\right) \text{ and } \left(\frac{dc'}{dT}\right), L \text{ and } L'$$

from LE CHATELIER's equation (see above par. 1) in our case, where they refer to the modifications IV and III of ammonium nitrate

$\left(\frac{dc}{dT}\right)_{IV}$ and $\left(\frac{dc}{dT}\right)_{III}$, respectively Q_{IV} and Q_{III} , we find:

¹⁾ These Proceedings 27, 65 (1924); Zeitschr. f. physik. Chemie 109, 81 (1924).

TABLE 4.
Solubility of Ammonium nitrate, Modification III, in water.

Temp.	Period of shaking in hours	v_c found	v_c mean	Solubility; gr. of salt per 100 gr. of solution			$c_{\text{calc.}} - c_{\text{found}}$
				c_{found} fr. v_c	c mean found	c calcul- ated	
33°.00	15	0.75638 *)		71.11			± 0.00
	18	0.75636	0.75636	71.12	71.12	71.12	
	18	0.75635		71.12			
36°.00	12	0.75268 *)		72.22			— 0.01
	18	0.75272	0.75271	72.20	72.21	72.20	
	18	0.75272		72.20			
39°.00	12	0.74915 *)		73.27			± 0.00
	18	0.74913	0.74914	73.28	73.27	73.27	
	18	0.74913		73.28			
42°.00	12	0.74564 *)		74.32			± 0.00
	18	0.74563	0.74563	74.32	74.32	74.32	
	18	0.74562		74.33			
45°.00	4	0.74222 *)		75.35			± 0.00
	5	0.74225	0.74223	75.34	75.34	75.34	
	5	0.74223		75.34			
48°.00	12	0.73885 *)		76.36			— 0.01
	24	0.73887	0.73886	76.35	76.35	76.34	
	24	0.73887		76.35			

*) signifies: starting from supersaturated solution.

From equation (4):

$$\left(\frac{dc}{dT}\right)_{IV} = 0.6106 - 2 \times 0.00297 \times 32.27 = 0.4189 \frac{\text{weight } \%}{\text{degree}}$$

From equation (6):

$$\left(\frac{dc}{dT}\right)_{III} = 0.4384 - 2 \times 0.00111 \times 32.27 = 0.3668 \frac{\text{weight } \%}{\text{degree}};$$

therefore

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} = \frac{0.4189}{0.3668} = 1.14^2 .$$

E. Calculation of $\frac{Q_{IV}}{Q_{III}}$ at the Transition temperature.

17. By means of an adiabatic, electrical method for the intermediate heats of solution of modification IV and III at their point of transition ($32^{\circ}.3$) ERNST COHEN and W. D. HELDERMAN ¹⁾ have found:

$$(Q_i)_{IV} = -5910 + 83.057 c - 0.73476 c^2 + 0.00224 c^3 . . . (7)$$

and

$$(Q_i)_{III} = -5510 + 83.057 c_1 - 0.73476 c_1^2 + 0.00224 c_1^3 . . . (8)$$

in which c , respectively c_1 , represents the concentration of a solution of ammonium nitrate (sum = 100), in which one molecule of the modification in question is dissolved.

For the transition temperature ²⁾ $c = c_1 = 70.93$; by means of the equations (7) and (8) we then find:

$$Q_{IV} = -2917 \text{ gramcalories}$$

and

$$Q_{III} = -2517 \text{ gramcalories}$$

so:

$$\frac{Q_{IV}}{Q_{III}} = \frac{2917}{2517} = 1.15^{\circ} .$$

F. Experimental proof of the relation of LE CHATELIER.

18. Whereas in par. 16 was found:

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} = 1.14^2$$

we find in par. 17

$$\frac{Q_{IV}}{Q_{III}} = 1.15^{\circ}$$

which proves experimentally the exactness of LE CHATELIER's relation.

¹⁾ These Proceedings 28, 1 (1924); Zeitschr. f. physik. Chemie 113, 145 (1924).

²⁾ We take here $32^{\circ}.27$ C., the point of intersection of the curves of solubility, therefore the value which was found in par. 15, instead of $32^{\circ}.3$, the value determined by COHEN and KOOY by dilatometric way.

G. MONDAIN MONVAL's investigation.

1. The solubility determinations.

19. The results of his solubility determinations are given in table 5

TABLE 5.
Solubility of NH_4NO_3 at different temperatures (MONDAIN MONVAL).

Temperature	Gr. NH_4NO_3 in 100 gr. of water	Molecular concentration C. (sum = 1)
26°.7	215.0	0.3257
28.6	223.6	0.3344
29.4	227.1	0.3379
30.4	232.5	0.3431
30.8	234.5	0.3450
32.2	241.2	0.3515
32.9	244.4	0.3544
33.8	248.3	0.3581
35.3	255.6	0.3648
36.0	259.0	0.3679
39.2	274.5	0.3814

By means of these experimental results, which give a point of intersection of the solubility curves of modification IV and III at $31^\circ.8$ MONDAIN MONVAL calculates (without further explanation) for the quotient

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} \text{ the value of } 1.17, \text{ at the temperature mentioned.}$$

By means of the method of least squares we find, however, from columns 1 and 3 in table 5:

$$c_{IV} = 0.3354 + 0.00472(t-28.8) \dots \dots \dots (9)$$

and

$$c_{III} = 0.3664 + 0.00429(t-35.7) \dots \dots \dots (10)$$

Table 6 proves that the equations (9) and (10) are in very close agreement with the results of MONDAIN MONVAL.

TABLE 6.

Temperature	c_{found}	$c_{\text{calculated}}$	$(c_{\text{calc.}} - c_{\text{found}}) \times 10^4$
26°.7	0.3257	0.3255	- 2
28.6	0.3344	0.3345	+ 1
29.4	0.3379	0.3382	+ 3
30.4	0.3431	0.3430	- 1
30.8	0.3450	0.3448	- 2
31.8	0.3500	0.3496	- 4
32.2	0.3515	0.3514	- 1
32.9	0.3544	0.3544	\pm 0
33.8	0.3581	0.3582	+ 1
35.3	0.3648	0.3647	- 1
36.0	0.3679	0.3677	- 2
39.2	0.3814	0.3815	+ 1

The point of intersection of the curves (9) and (10) is 31°.8, while, by means of these equations we find:

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} = \frac{0.00472}{0.00429} = 1.10$$

and *not* 1.17, which figure is given by MONDAIN MONVAL.

20. We are of opinion that it is superfluous to trace the reason which has led to such a great divergence from the figure (1.14) found by us. We only wish to observe that MONDAIN MONVAL finds values for the solubility at all the temperatures investigated by him, which lie far below ours, and as we have always attained equilibrium of solution with highly different periods of shaking, from above as well as from below, at which we found identical values, whereas he, with far shorter periods of shaking (during which the temperature was but a short time above the temperature of equilibrium) thought to have reached equilibrium, it is very probable that in his investigations this has not been the case.

The way in which MONDAIN MONVAL prepares the saturated solutions for analysis (filtering the excess of salt through a previously heated funnel, during which crystallisation is not excluded) may also have been one of the causes of his too low results. Then he has been experimenting

within too small ranges of temperature, so that the values of $\left(\frac{dc}{dT}\right)_{IV}$ and $\left(\frac{dc}{dT}\right)_{III}$ are doubtful.

2. Determination of the fictitious heats of solution Q_{IV} and Q_{III} .

21. Now that we have obtained our results we will not enter into a discussion of the particulars of MONDAIN MONVAL's method to find $\frac{Q_{IV}}{Q_{III}}$, and only wish to observe, that the way, in which he has measured the intermediate heats of solution of the two modifications in solutions of different concentrations, has been a rather rough one. COHEN and HELDERMAN¹⁾ have determined those values by means of a highly perfected, calorimetric method, with an accuracy of 0.3 per cent. Tables 7 and 8 show that the divergencies between the values of MONDAIN MONVAL and those of COHEN and HELDERMAN are not inconsiderable.

MONDAIN MONVAL calculates the quotient $\frac{Q_{IV}}{Q_{III}}$ by means of the values found by him $Q_{IV} = -2.93$ and $Q_{III} = -2.53$, whereas the investigation by COHEN and HELDERMAN has given the values -2.917 and -2.517 .

The value of $\frac{Q_{IV}}{Q_{III}}$, calculated by MONDAIN MONVAL happens to be the same as the value furnished by the much more accurate figures of COHEN and HELDERMAN, viz. 1.16.

TABLE 7.

Intermediate heats of solution of Ammonium nitrate, Modification IV, according to MONDAIN MONVAL and according to COHEN and HELDERMAN, at 28° and 32°. 3 respectively.

Experiment	Initial conc. in gr. p. 100 gr. of solut.	Final conc. in gr. p. 100 gr. of solut.	Mean conc. in gr. p. 100 gr. of solut.	Intermed. heat of solution in Kgr. cal. per mol.		Difference
				MONDAIN MONVAL	COHEN— HELDERMAN	
1	0	2.23	1.11	- 5.90	- 5.819	+ 0.08
2	20	22.03	21.01	- 4.62	- 4.468	+ 0.15
3	50	50.91	50.46	- 3.33	- 3.302	+ 0.03
4	56.9	57.53	57.22	- 3.19	- 3.144	+ 0.05
5	66.6	67.18	66.89	- 3.02	- 2.972	+ 0.05

¹⁾ These Proceedings 28, 1 (1924); Zeitschr. f. physik. Chemie 113, 145 (1924).

TABLE 8.

Intermediate heats of solution of Ammonium nitrate, Modification III, according to MONDAIN MONVAL and according to COHEN and HELDERMAN, at 36° and 32°.3 respectively.

Experiment	Initial conc. in gr. p. 100 gr. of solut.	Final conc. in gr. p. 100 gr. of solut.	Mean conc. in gr. p. 100 gr. of solut.	Intermed. heat of solution in Kgr. cal. per mol.		Difference
				MONDAIN MONVAL	COHEN— HELDERMAN	
1	0	2.57	1.28	— 5.35	— 5.405	— 0.06
2	34.8	35.94	35.37	— 3.44	— 3.392	+ 0.05
3	57.0	57.71	57.36	— 2.86	— 2.741	+ 0.12
4	70.0	70.37	70.19	— 2.54	— 2.525	— 0.01

22. From the investigation of MONDAIN MONVAL results:

$$\frac{\left(\frac{dc}{dT}\right)_{IV}}{\left(\frac{dc}{dT}\right)_{III}} = 1.10 \quad \text{en} \quad \frac{Q_{IV}}{Q_{III}} = 1.16.$$

A satisfactory experimental testing of the "law of tangents" is therefore out of the question.

Summary.

In the above paper was shown that the experimental testing of the "Law of Tangents" of LE CHATELIER by MONDAIN MONVAL has led to unsatisfactory results, in consequence of insufficient accuracy of the data necessary for such a proof. An agreement between theory and experiment, satisfactory in every respect, was found by employing more accurate methods.

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VAN 'T HOFF *Laboratory.*