Measurement of mercurous chloride vapor pressure

Komla Oscar Awitor,* Laurent Bernard, Bernard Coupat, Jean Paul Fournier and Philippe Verdier

Laboratoire des Sciences et Matériaux pour l'Electronique et d'Automatique (LASMEA, CNRS UMR 6602), Université Blaise Pascal, Complexe Scientifique des Cézeaux, 63177 Aubière cedex, France. Fax: +33 4 73 40 73 40; E-mail: awitor@lasmea.univ-bpclermont.fr

Received (in Montpellier, France) 7th January 2000, Accepted 27th March 2000

The composition of mercurous chloride vapor is not well known despite the studies devoted to it. This paper is a study of calomel vapor pressure based on atomic absorption spectroscopy of mercury in the vapor phase. The results obtained prove that in the vapor phase below 473 K, mercurous chloride is completely dissociated into mercury and mercuric chloride, and resultant vapor pressure measurements correspond closely to those obtained with the Knudsen effusion method.

Mercurous chloride is a promising material for acousto-optical applications, crystals of good quality being obtained by vapor phase growth.[1] A knowledge of the composition of the vapor phase is needed for good growth control. Since mercury is in its monoatomic form in the vapor phase, the mercury pressure in calomel vapor can be measured by atomic absorption spectroscopy. This has allowed the vapor pressure of calomel to be determined and thus confirms that in the vapor phase, at temperatures between 393 and 473 K, calomel vapor is completely dissociated into mercury and mercuric chloride.

Experimental

Measurement principle

In a recent study,[2] a new synthetic method for calomel was put forward and the vapor pressure of the compound between 353 and 453 K was measured. Mass spectroscopy analysis studies allowed us to conclude that the dissociation of mercurous chloride in the vapor phase was complete. These conclusions are consistent with the measurements of Opperman *et al.*,[3] who worked in the temperature range above 473 K, but contradict those of Singh *et al.*,[4] who analyzed their results taking non-dissociative sublimation into account.

Mercury vapor being monoatomic, it is possible to measure the mercury vapor pressure in a sealed ampoule by atomic absorption spectroscopy, at a wavelength of 253.7 nm. Taking into account that the equilibrium:

$$\mathrm{Hg_2Cl_2}_{\,\mathrm{solid}} \Leftrightarrow \mathrm{Hg_{gas}} + \mathrm{HgCl_2}_{\,\mathrm{gas}} \qquad (1)$$

governs calomel dissociation, the calomel vapor pressure must be double that of mercury. Unfortunately, mercurous chloride always contains traces of mercuric chloride. Consequently, the measured mercury pressure will depend on the amount of mercuric chloride, the calomel mass used, and the volume of the ampoule. In a recent study,[5] we accurately measured mercuric chloride pressure in the 343–453 K range. If in addition to calomel, we also add to the measurement cell a sufficient amount of mercuric chloride to obtain the equilibrium:

$$\mathrm{HgCl_2}_{\,\mathrm{solid}} \Leftrightarrow \mathrm{HgCl_2}_{\,\mathrm{gas}} \qquad (2)$$

then the measurement of mercury vapor pressure will allow us to determine the calomel vapor pressure, assuming the existence of equilibrium (1). The measurement of mercury pressure in the vapor phase will demonstrate that calomel vapor is dissociated and coincidence of the pressure values obtained by this method with those measured with the Knudsen effusion method[2] will confirm that the dissociation is complete.

Experimental device

This device is based on the flameless atomic absorption method[6] used for water analysis. The measurement cell shown in Fig. 1 is equipped with two quartz windows (wavelength equal to 253.7 nm); it is then put inside an electrical tubular oven, itself equipped with quartz windows to provide better thermal homogeneity. Thermal control is provided by a type K thermocouple regulator. Considering the high absorbance of mercury vapor, the cell thickness has been limited to 5 mm. We have used a Pye Unicam atomic absorption spectrometer equipped with a mercury hollow lamp. The empty device has an absorbance of 0.22.

Calibration

Firstly, our apparatus was calibrated using Aldrich Chemical Company Inc. mercury 99.9995%. Among different formulae

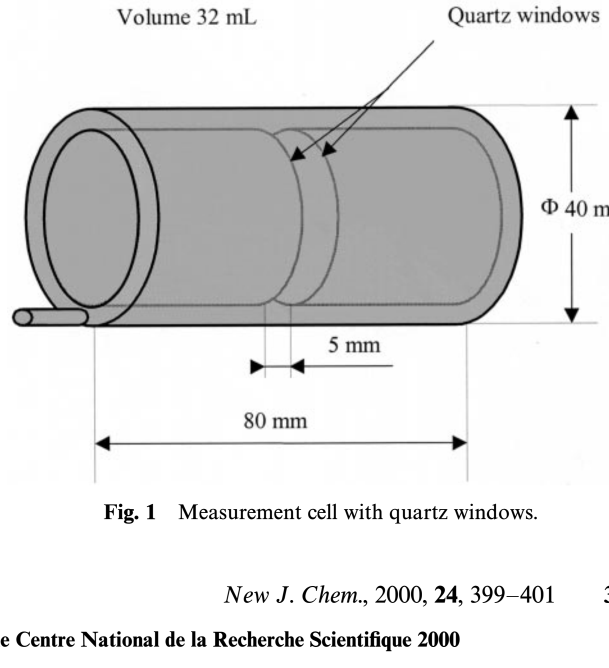

Fig. 1 Measurement cell with quartz windows.

DOI: 10.1039/b000238k

Table 1 Calibration of the device with mercury

T/K	Absorbance	[Hg]/atom m^{-3}
292.5	0.369	6.777×10^{-5}
298.2	0.454	1.074×10^{-4}
300.1	0.490	1.247×10^{-4}
306.1	0.631	1.975×10^{-4}
312.1	0.825	3.073×10^{-4}
315.1	0.942	3.807×10^{-4}
318.1	1.040	4.699×10^{-4}
321.1	1.165	5.775×10^{-4}
324.1	1.350	7.070×10^{-4}
326.1	1.430	8.074×10^{-4}
328.1	1.573	9.206×10^{-3}
330.1	1.550	1.048×10^{-3}
333.1	1.680	1.269×10^{-3}

available in the literature for mercury vapor pressure, we chose that of Alcock *et al.*:[7]

$$\ln(P_{\mathrm{Hg}}/\mathrm{Torr}) = 18.4133 - \frac{7345.2}{(T/\mathrm{K})} \qquad (3)$$

Table 1 presents the measured absorbance *vs.* absolute temperature and the calculated mercury concentration in the vapor.

The variation of the absorbance *vs.* mercury concentration is not linear, as shown in Fig. 2. In order to obtain the mercury concentration from the absorbance measurements, we used a second-degree polynomial smoothing.

$$A = -7.62 \times 10^5[\mathrm{Hg}]^2 + 2.09 \times 10^3[\mathrm{Hg}] + 0.240 \qquad (4)$$

The straight line in Fig. 2 is an extrapolation of the measurements achieved at low mercury concentrations.

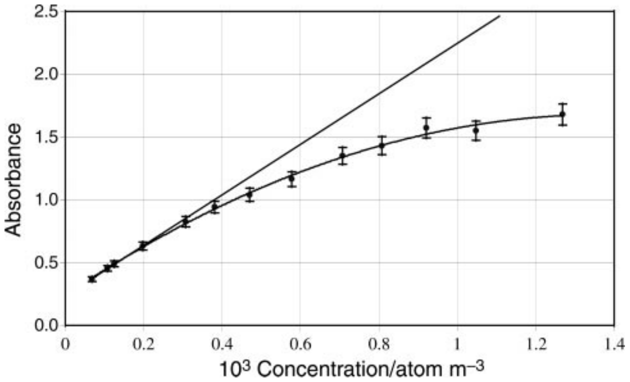

Fig. 2 Calibration of the measurement cell (absorbance *vs.* mercury concentration).

Results and discussion

We used Aldrich Chemical Company Inc. commercial reagents. Table 2 shows the measurements obtained by adding 100 mg of calomel (>99.5%) and 10 mg of mercuric chloride (99.999%) to the cell. The mercuric chloride pressure is obtained from a formula derived from ref. 5:

$$\ln(P_{\mathrm{HgCl_2}}/\mathrm{Pa}) = 28.17 - \frac{9531}{(T/\mathrm{K})} \qquad (5)$$

The accuracy of the calomel pressure is difficult to evaluate; it is certainly less accurate for temperatures above 450 K, because of the shape of the calibration curve and also because the formula used for mercuric chloride pressure corresponds to the temperature range 343–453 K. For temperatures between 393 and 413 K, the mercury vapor absorbance is very low; the use of a thicker cell would increase accuracy and allow lower temperature measurements.

The results are reported in Fig. 3. Napierian logarithm smoothing *vs.* reciprocal temperature leads to:

$$\ln(P_{\mathrm{Hg_2Cl_2}}/\mathrm{Pa}) = 26.5 - \frac{10027}{(T/\mathrm{K})} \qquad (6)$$

with a correlation coefficient equal to 0.998. This equation can be compared with that in ref. 2:

$$\ln(P_{\mathrm{Hg_2Cl_2}}/\mathrm{Pa}) = 27.7 - \frac{10571}{(T/\mathrm{K})} \quad \text{for } T = 343\text{–}453 \text{ K} \qquad (7)$$

The difference between the two results is essentially due to measurements obtained at 393 and 403 K. If these two values are removed, the smoothing becomes:

$$\ln(P_{\mathrm{Hg_2Cl_2}}/\mathrm{Pa}) = 27.5 - \frac{10478}{(T/\mathrm{K})} \qquad (8)$$

The agreement in the calomel vapor pressures obtained by atomic absorption measurements of mercury vapor and the Knudsen effusion method allows us to conclude that the dissociation of calomel into mercury and mercuric chloride in the

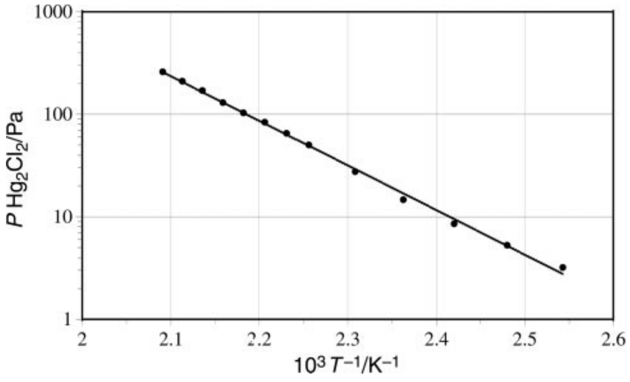

Fig. 3 Calomel pressure *vs.* reciprocal temperature.

Table 2 Mercurous chloride vapor pressure derived from absorbance measurements and mercuric chloride vapor pressure

T/K	Absorbance	$P(HgCl_2)$/Pa	[Hg]/atom m^{-3}	$P(Hg_2Cl_2)$/Pa
393.2	0.272	50.8	1.55×10^{-5}	3.2
403.2	0.286	92.6	2.22×10^{-5}	5.3
413.2	0.307	164.2	3.25×10^{-5}	8.6
423.2	0.351	283.2	5.41×10^{-5}	14.7
433.2	0.463	476.3	1.11×10^{-4}	27.6
443.2	0.663	782.6	2.20×10^{-4}	50.3
448.2	0.776	995	2.86×10^{-4}	65.1
453.2	0.902	1258	3.64×10^{-4}	83.1
458.2	1.020	1583	4.44×10^{-4}	104
463.2	1.157	1981	5.46×10^{-4}	129
468.2	1.385	2468	7.53×10^{-4}	170
473.2	1.524	3060	9.23×10^{-4}	211
478.2	1.628	3778	1.11×10^{-3}	259

vapor phase is complete for temperatures below 473 K. These results are consistent with the conclusions of Opperman *et al.*[3] and the mass spectral study[2] of calomel vapor.

References

1 G. J. Rosasco, H. S. Parker, R. S. Roth, R. A. Forman and W. S. Brower, *J. Phys. C: Solid State Phys.*, 1978, **11**, 35.

2 K. O. Awitor, L. Bernard, O. Bonnin, B. Coupat, J. P. Fournier and P. Verdier, *Can. J. Chem.*, 1999, **77**, 243.

3 H. Oppermann, C. Barta and J. Trnka, *Z. Anorg. Allg. Chem.*, 1989, **568**, 187.

4 N. B. Singh, M. Gottlieb, R. H. Hoppkins, R. Mazelsky, W. M. B. Duval and M. E. Glicksman, *Prog. Cryst. Growth Charact.*, 1993, **27**, 201.

5 O. Bonnin, K. O. Awitor, J. P. Badaud, L. Bernard, B. Coupat, J. P. Fournier and P. Verdier, *J. Phys. III*, 1997, **7**, 311.

6 J. Rodier, *L'Analyse de l'Eau*, Dunod, Bordas, Paris, 7th edn., 1984, pp. 321–324.

7 C. B. Alcock, V. P. Itkin and M. K. Horrigan, *Can. Metallur. Quart.*, 1984, **23**, 309.