

Vapour Pressure of Barium Metal & Study of the Equilibrium Reaction $\text{Ba}(g) + \text{BaCl}_2(c) = 2\text{BaCl}(g)$ at High Temperature*

M. P. KULKARNI & V. V. DADAPE†

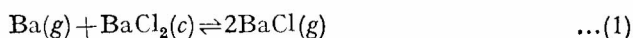
National Chemical Laboratory, Poona 8

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The vapour pressure of barium metal has been determined at temperatures in the range 1160-1333°K employing a transpiration technique. The second law calculations yield for the heat of sublimation (ΔH_{298}) a value of 40.43 ± 4.94 kcal mole⁻¹, which compares favourably with third law value 43.54 ± 0.57 kcal mole⁻¹. The equilibrium reaction $\text{Ba}(g) + \text{BaCl}_2(c) = 2\text{BaCl}(g)$ has been investigated between 1210° and 1305°K employing a flow method. Over the temperature range ΔH_{r1258} is found to be 77.76 ± 8.97 kcal mole⁻¹. The heat of formation of $\text{BaCl}(g)$ (ΔH_{f298}) derived from this yields a value of -40.29 ± 8.97 kcal mole⁻¹ by the second law which is in good agreement with the corresponding third law value of -43.67 ± 1.09 kcal mole⁻¹. The entropy of the reaction (ΔS_{r1258}) is calculated to be 49.26 ± 7.12 e.u.

THOUGH the existence of barium monochloride has been reported by many investigators, the heat of formation of gaseous BaCl has not been determined experimentally. Available literature values are only the estimates based on the dissociation energy of the $\text{BaCl}(g)$ molecule. Herzberg¹ reported the dissociation energy (D_0°) of the barium sub-halide as 2.7 eV whereas Gaydon² obtained a value 5.0 ± 0.4 eV. Gurvich³ reported the dissociation energy D_0° of BaCl as 118 ± 5.0 kcal mole⁻¹. Using heat of sublimation of barium⁴ as 41.74 kcal mole⁻¹ and the heat of formation of ideal monoatomic chlorine as 28.94 kcal mole⁻¹ (refs. 5 and 6) the values obtained for the heat of formation of $\text{BaCl}(g)$ are $+8.58$, -44.32 ± 9.2 , -47.32 ± 5.0 kcal mole⁻¹ respectively. Feber⁷ calculated the heat of formation at 298.15°K of the gaseous barium monochloride as -49.0 kcal mole⁻¹.

Quill in his book⁸ mentions that Eastmann and coworkers claim that there are no stable solid sub-halides, and Cubicciotti reported the phase diagram for $\text{Ba}-\text{BaCl}_2$, $\text{Ca}-\text{CaCl}_2$ and $\text{Sr}-\text{SrCl}_2$ systems. In all these cases the phase diagrams show no evidence of solid sub-halide though there was appreciable solubility of the metal in the halide. The existence of bands due to $\text{BaCl}(g)$ was reported by King⁹ in 1905 and Parker¹⁰ in 1934. In view of the non-availability of any experimental value for the heat of formation of $\text{BaCl}(g)$ it was thought worth while to study the equilibrium reaction



at high temperature. The vapour pressure of $\text{Ba}(l)$ in equilibrium with $\text{Ba}(l)$ was also evaluated.

Vapour pressure of Ba metal by the boiling point method was determined for the first time in 1924 (ref. 12) and later in 1935 (ref. 13) employing Knudsen effusion method. In these studies, the purity of the metal sample was not quite high and

also it was difficult to obtain uniform temperatures of the effusion chambers. The results, therefore, were influenced by these drawbacks¹⁴. It was therefore necessary to study the vaporization of Ba metal at high temperatures.

The present study includes (i) vaporization of Ba metal at temperatures between 1160° and 1330°K and (ii) equilibrium reaction of $\text{Ba}(g)$ with $\text{BaCl}_2(c)$ at temperatures between 1210° and 1305°K .

Materials and Methods

Barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), BDH Analar grade, was dehydrated in a stream of HCl at 400°C for 2 hr using purified nitrogen as carrier gas. The dichloride was chemically analysed for chloride and barium by standard methods of analysis. The purity was found to be more than 99.9%. The anhydrous dichloride was freshly prepared for each experiment.

Ba metal (Fluka, AG, Switzerland) was chemically analysed in a dry box (having argon atmosphere). The purity was found to be more than 99.5%.

Argon was used as a carrier gas. Impurities like oxygen, nitrogen, carbon dioxide and moisture were removed by methods described earlier by Rao¹⁵. In addition titanium metal at 1000°C was used to remove traces of oxygen and nitrogen.

Apparatus and procedure—The experimental set-up consists of a tube furnace which can be easily heated in a furnace in the range 1100° to 1300°K having two constant temperature zones of about 20 cm length. Transparent silica boats were used as containers for the solid materials and mullite tube with standard glass joints was used as the reaction tube. Temperatures were measured by means of calibrated chromel-alumel thermocouples and a flow meter was employed to measure the rate of flow of carrier gas.

Results and Discussion

Vaporization of Ba metal—The barium metal was cut into small pieces under petroleum. The pieces were quickly and carefully dried with filter

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†Present address: Development Manager, M/s Dharamsi Morarji Chemicals Ltd, P.O. Ambarnath, Thane.

paper and then transferred to the boat. These operations were carried out in a dry box through which argon gas was passed.

The reaction tube was completely flushed with argon gas. After attaining the required constant temperature and maintaining desired flow of argon gas, the boat containing barium metal was introduced from the downstream end. The experiments were carried out for 1 hr. After completing the reaction the boat was pushed to a chamber containing dry argon and then weighed. The vaporization was carried out at different temperatures and the results are recorded in Table 1. The vapour pressure data have been employed in the study of the equilibrium reaction (1).

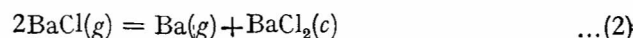
Study of the equilibrium reaction—The experimental set-up was the same as described above. The temperature of the zone in which the vapour of Ba metal was generated was maintained as 1200°K and other zone was kept at the desired temperature for the reaction. Refractory plugs of suitable sizes were introduced at the proper points to act as radiation shields and diffusion barriers without which the equilibrium could not be easily attained.

To study the equilibrium reaction the argon gas rate was regulated to the desired value (3.1 to 3.3 litres/hr) and the experiment was started by pushing the boats containing metal and metal chloride in the respective zones. Experiments were carried out in the temperature range 1210-1305°K and the results are recorded in Table 2. After continuing the run for a definite time (1 hr) the boat containing barium metal was pushed out of the hot zone; thereby arresting the reaction. The heating was then stopped, the system allowed to cool in argon and both the boats were weighed.

Further the vapour pressure of BaCl₂ at temperature studied is quite negligible. But when the

vapour of barium is passed over BaCl₂, a loss in BaCl₂ was observed (due to the formation of BaCl). This loss combined with the observation of BaCl₂ and Ba (from BaCl) on a cold finger conclusively prove the formation of BaCl.

Identification of the gaseous products was carried out by condensing them on a silica cold finger. After the reaction the deposit on the cold finger on chemical analysis showed the presence of BaCl₂. It is possible that the deposit of BaCl₂(c) may be due to the disproportion of BaCl(g) in accordance with Eq. (2)



The weight loss data were used to calculate the partial pressures of BaCl(g) and Ba(c) using the following reactions:

$$P_{\text{BaCl}} = n_a \frac{RT}{V_r} \quad \dots(3)$$

$$P_{\text{Ba}} = n_b \frac{RT}{V_r} \quad \dots(4)$$

where n_a and n_b are the number of moles of BaCl and Ba respectively. The equilibrium constant K_p was calculated from Eq. (5)

$$K_p = \frac{(P_{\text{BaCl}})^2}{P_{\text{Ba}}} \quad \dots(5)$$

The free energy and heat of reaction at various temperatures were calculated employing Eqs. (6) and (7)

$$\Delta G^\circ = -RT \ln K \quad \dots(6)$$

$$\frac{\Delta H_{298}^\circ}{T} = -R \ln K - \frac{G_T^\circ - H_{298}^\circ}{T} (\text{Prod}) + \frac{G_T^\circ - H_{298}^\circ}{T} (\text{react}) \quad \dots(7)$$

TABLE 1 — VAPORIZATION OF Ba(l) = Ba(g) AND THIRD LAW HEATS

Temp. °K	Argon gas passed litre/hr	Ba metal transported (mg)	$P \times 10^3$ atm.	$-RT \ln K_p$ kcal mole ⁻¹	Δ_{fef} cal mole ⁻¹	$T\Delta_{fef}$ kcal mole ⁻¹	ΔH_{298}° kcal mole ⁻¹
1160	3.09	17.0	0.9794	15.97	23.50	27.26	43.23
1195	3.09	22.0	1.2675	15.84	23.38	27.93	43.77
1225	2.90	28.0	1.7188	15.49	23.31	28.55	44.04
1240	2.76	46.0	2.0671	14.34	23.27	28.85	43.19
1273	2.40	67.0	4.9698	13.42	23.18	29.51	42.93
1333	2.10	74.0	6.2733	13.43	23.02	30.68	44.11

Duration of experiment = 1 hr.

Av. = 43.54 ± 0.57.

TABLE 2 — TRANSPIRATION DATA AND RELATED THIRD LAW HEATS FOR THE REACTION Ba(g) + BaCl₂(c) = 2BaCl(g)

Temp. °K	Argon gas passed litre/hr	Ba(g) passed (mg)	BaCl ₂ (c) transported (mg)	$P \times 10^{-3}$ BaCl(g) atm.	$-\log K_p$	$-RT \ln K$ kcal/mole	$\Delta H_{r,298}^\circ$ kcal/mole ⁻¹	ΔH_{298}° BaCl(g) kcal mole ⁻¹
1210	3.00	22.0	11.5	0.9009	3.2072	17.75	74.88	43.59
1235	3.09	24.0	13.5	1.0259	3.1185	17.62	75.76	43.15
1255	3.21	53.0	29.0	2.1217	2.8150	16.16	75.04	43.51
1270	3.00	22.0	25.5	1.9568	2.5326	14.71	74.09	43.98
1285	2.90	17.0	25.5	2.0646	2.3888	14.04	73.97	44.05
1305	3.30	64.0	58.0	4.1269	2.3068	13.77	74.47	43.79

Duration of each run is 1 hr; ΔH_{298}° BaCl(g) = 43.67 ± 1.09 kcal mole⁻¹ (av.); ΔH_{298}° of Ba(g) = 43.54 ± 0.57 taken from third law of Table 2; and generation temperature of Ba(g) = 1200°K.

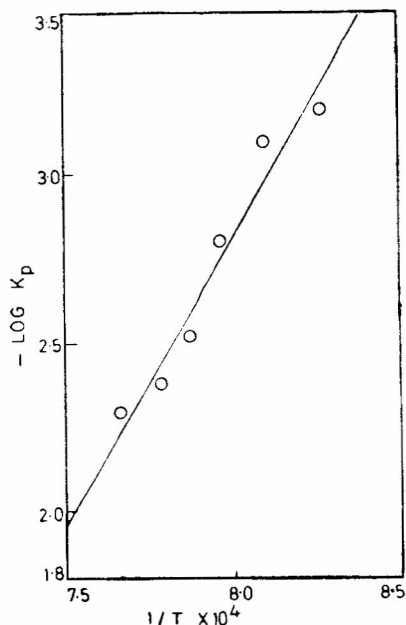


Fig. 1 — Plot of $-\log K_p$ versus $1/T$ for the reaction $\text{Ba}(g) + \text{BaCl}_2(c) \rightleftharpoons 2\text{BaCl}(g)$

The experimental results have been summarized in Table 2. The values of $\log K_p$ are plotted against the reciprocal of the absolute temperature (Fig. 1). From the slope of the plot the heat of reaction (ΔH_{r1258}) was found to be 77.76 ± 8.97 kcal mole⁻¹. According to King and Kelley¹¹ the change in C_p value is 9.01 kcal mole⁻¹. When this value is integrated between the limits 298° and 1258°K the value of 8.65 kcal mole⁻¹ is obtained. This when added to the value of ΔH_{r1258} yields 86.41 ± 8.97 kcal mole⁻¹ for ΔH_{r298} .

The third law calculation is carried out using free energy functions which are calculated at desired temperature using entropy and $H_T - H_{298}$ values tabulated by King and Kelley¹¹. The average experimental value for the heat of reaction at 298°K is 74.70 ± 1.64 kcal mole⁻¹.

Vapour pressure data of Ba — Employing the Vant Hoff's reaction,

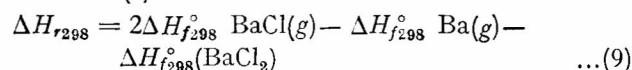
$$\frac{d \ln P}{d(1/T)} = \frac{\Delta H_v^\circ}{R} \quad \dots(8)$$

the heat of vaporization of Ba(c) has been determined from the values of $\log P$ and $1/T$. The constants from the least square line led to a value of 36.80 ± 4.94 kcal mole⁻¹ for ΔH_{vap}° at 1246°K. It represents the mean value over the temperature range studied. According to Stull and Sinke⁴ the

change in C_p is 1.89 kcal mole⁻¹. This difference in the C_p when integrated between the limits 298° and 1246°K gives a value of 1.79 kcal mole⁻¹. This when added to the above value of heat of sublimation at 1246°K yields $\Delta H_{298}^\circ = 38.60 \pm 4.94$ kcal mole⁻¹. Adding the heat of fusion⁴ $\Delta H_{f298}^\circ = 1.83$ kcal mole⁻¹, ΔH_{298}° has a value of 40.43 ± 4.94 kcal mole⁻¹.

For the calculation by third law method, Δ_{fef} has been obtained employing values of Stull and Sinke⁴, for Ba(g) and Ba(c); ΔH_r is calculated from experimentally determined free energy (ΔG_T°). From the value of ΔH_r , ΔH_{f298}° of Ba(g) is found to be 43.54 ± 0.57 kcal mole⁻¹.

Equilibrium reaction — In the study of equilibrium reaction (1)



The second law value for the heat of formation of BaCl(g) ΔH_{f298}° (-40.29 ± 8.97 kcal mole⁻¹) is in good agreement with that obtained by the third law ($\Delta H_{f298}^\circ = -43.67 \pm 1.09$ kcal mole⁻¹). The experimentally obtained value for the heat of formation for BaCl(g) compares well with that calculated from the dissociation² ($\Delta H_{f298}^\circ = -44.32 \pm 9.2$ kcal mole⁻¹).

The entropy of the reaction was found to be 49.26 ± 7.13 e.u. at 1258°K.

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