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Vapor Pressures of the MgI_2–H_2O–I_2 System

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Vapor pressures for the MgI_2–H_2O–I_2 system were measured up to about 150 kPa. The mole ratio of H_2O to MgI_2 and that of I_2 to MgI_2 were varied from 10.862 to 42.432 and from 0.01 to 8.0, respectively. An empirical method was suggested for correlating the vapor pressures in the ternary system. The agreement between the experimental and calculated results was very good.

Introduction

The concentrating of aqueous solutions containing I_2 and MgI_2 is an important process in the magnesium–iodine cycle for thermochemical hydrogen production (*1*). In order to design this evaporation process, the vapor pressures of the MgI_2–H_2O–I_2 system were measured as the fundamental data.

Experimental Section

Vapor pressure data were obtained by means of the equipment and procedures described previously (*2*) except for two modifications: (a) the volume of the sample container was changed from 30 to 100 cm^3 in order to minimize the change of liquid-phase composition during the evacuation of the air from the system and (b) the liquid-phase composition was determined from the charged weights of the dried pure I_2 and MgI_2 aqueous solution of known concentration. The change of the composition owing to evacuation was within 0.4% and that owing to partition of I_2 and H_2O between both phases was within 0.4%. Therefore, the total error of the liquid-phase composition was judged to be within 0.8%.

Results and Discussion

The vapor pressures of the MgI_2–n_1H_2O–n_2I_2 system were measured up to about 150 kPa, where n_1 is the mole ratio of H_2O to MgI_2 and n_2 is that of I_2 to MgI_2. The experiments were divided into three groups: (a) MgI_2–$10.862H_2O$–n_2I_2, (b) MgI_2–$21.301H_2O$–n_2I_2, and (c) MgI_2–$42.432H_2O$–n_2I_2. The experimental results are given in Table I. Figure 1 shows the relationship between p and n_2 at various temperatures, where p is the vapor pressure of the MgI_2–n_1H_2O–n_2I_2 system smoothed by the Antoine equation: $\log p = A + B/(T + C)$. In this figure the y intercept is the vapor pressue of the MgI_2–n_1H_2O system (p_1) and can be calculated by the method proposed by the authors (*3*). Most of the points for each temperature and n_1 lie on a straight line and so p was fitted by the least-squares relation

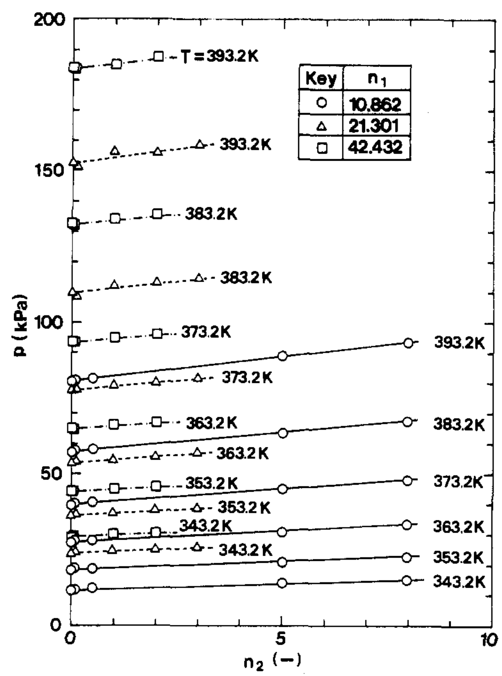

Figure 1. p as a function of n_2 for MgI_2–n_1H_2O–n_2I_2.

$$p = p_1 + \alpha n_2 \quad (1)$$

where α is the slope of the straight line. Furthermore, the relationship between α and n_1 is shown in Figure 2 from 343.2 to 393.2 K. The values of α were correlated by using the empirical equation

$$\alpha = \alpha_0 + \alpha_1 n_1^{1/2} + \alpha_2 n_1 \quad (2)$$

The parameters α_0, α_1, and α_2 at various temperatures are

Table I. Vapor Pressures of MgI_2-n_1H_2O-n_2I_2 Systems

T, K	p, kPa
n_1 = 10.862, n_2 = 0.099	
327.0	5.43
343.5	11.74
358.1	22.39
380.3	51.99
391.3	75.87
400.6	101.45
408.0	127.59
412.0	144.39
n_1 = 10.862, n_2 = 0.500	
331.3	6.85
347.2	14.30
358.2	22.69
370.5	36.60
382.0	55.53
393.3	81.39
401.8	107.45
403.9	114.02
408.6	131.97
n_1 = 10.862, n_2 = 5.018	
345.6	15.25
358.6	26.05
370.0	39.84
382.0	61.00
391.5	83.71
398.7	105.05
406.2	131.75
411.1	152.96
n_1 = 10.862, n_2 = 7.978	
354.3	23.54
366.2	36.96
374.1	49.29
381.4	63.50
389.4	82.46
396.4	103.36
402.9	125.33
408.8	149.58
n_1 = 21.301, n_2 = 0.099	
333.0	15.33
342.7	23.34
353.1	36.42
359.8	47.16
367.4	62.42
374.3	80.23
381.0	101.13
385.4	116.66
391.7	143.56
394.0	154.96

T, K	p, kPa
n_1 = 21.301, n_2 = 0.986	
322.2	9.53
336.0	17.72
352.3	35.59
360.2	48.69
365.6	59.57
370.1	70.70
374.1	81.43
378.5	95.06
n_1 = 21.301, n_2 = 1.998	
329.7	13.69
334.3	25.99
355.9	42.06
365.0	59.17
373.2	80.15
380.4	102.75
386.4	125.49
392.3	152.06
n_1 = 21.301, n_2 = 2.999	
330.2	14.18
344.2	26.42
356.0	42.88
367.5	66.62
377.1	93.14
384.1	118.40
389.3	139.90
n_1 = 42.432, n_2 = 0.010	
327.9	14.77
344.0	29.89
352.9	43.40
371.0	86.42
379.5	116.34
385.8	143.47
389.6	162.33
n_1 = 42.432, n_2 = 0.999	
324.3	13.18
334.6	20.65
350.5	40.50
367.8	78.17
373.2	95.08
378.9	115.58
384.2	137.61
n_1 = 42.432, n_2 = 2.000	
327.4	15.34
343.8	31.11
358.3	55.97
368.0	79.79
377.5	111.95
383.4	136.15

Table II. Parameters in Eq 2

T, K	α_0	α_1	α_2
343.2	-2.8021×10^{-2}	1.3306×10^{-1}	2.2126×10^{-3}
353.2	-3.5780×10^{-1}	3.6361×10^{-1}	-2.2576×10^{-2}
363.2	-8.2029×10^{-1}	6.7642×10^{-1}	-5.6586×10^{-2}
373.2	-1.4030	1.0609	-9.7504×10^{-2}
383.2	-2.0623	1.4857	-1.3970×10^{-1}
393.2	-2.7118	1.8911	-1.7303×10^{-1}

given in Table II. The mean deviation between the experimental data and the calculated results by eq 1 and 2 was 0.25 kPa and the maximum deviation was 0.66 kPa for the MgI_2-21.301H_2O-0.986I_2 system.

To check the applicability of this correlation, the vapor pressures were measured for the MgI_2-28.893H_2O-1.024I_2 system and compared with the calculated values. The results are presented in Table III, where p(exptl) is the vapor pressure smoothed by the Antoine equation. The agreement was very good.

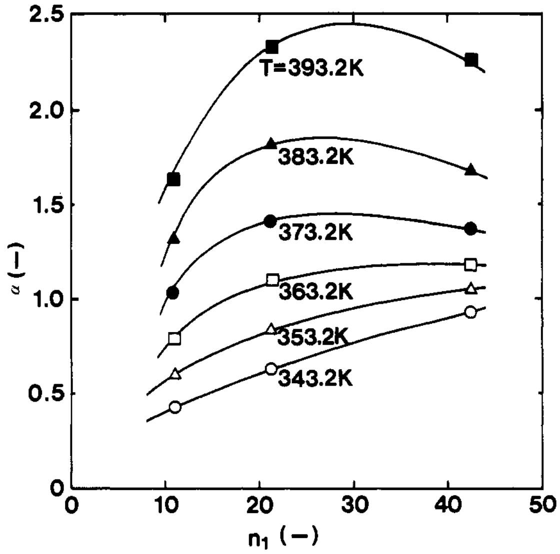

Figure 2. Relation between α and n_1 for MgI_2-n_1H_2O-n_2I_2.

Table III. Comparison between p(exptl) and p(calcd) System

T, K	p(exptl),[a] kPa	p(calcd), kPa	dev, kPa
343.2	27.34	27.38	0.04
353.2	41.31	41.42	0.11
363.2	61.00	61.10	0.10
373.2	88.19	88.08	-0.11
383.2	125.06	124.36	-0.70

[a] p(exptl) is the vapor pressure smoothed by the Antoine equation.

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Glossary

A,B,C	constants of the Antoine equation
n_1	mole ratio of H_2O to MgI_2
n_2	mole ratio of I_2 to MgI_2
p	vapor pressure of MgI_2-n_1H_2O-n_2I_2 system, kPa
p_1	vapor pressure of MgI_2-n_1H_2O system, kPa
T	temperature, K
α	slope of the straight line expressed by eq 1
$\alpha_0,\alpha_1,\alpha_2$	parameters in eq 2

Registry No. MgI_2, 10377-58-9; I_2, 7553-56-2.

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