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A Study of Nonstoichiometric Empirical Formulas for Semiconductive Metal Oxides

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An empirical formula for semiconductive metal oxides is proposed relating nonstoichiometric value x to a temperature or an oxygen partial pressure such that experimental data can be represented more accurately by the formula than by the well-known Arrhenius-type equation. The proposed empirical formula is $\log x = A + B\cdot 1000/T + C\cdot \exp(-D\cdot 1000/T)$ for a temperature dependence and $\log x = a + b\cdot \log P_{O_2} + c\cdot \exp(-d\cdot \log P_{O_2})$ for an oxygen partial pressure dependence. The A,B,C,D and a,b,c,d are parameters which are evaluated by means of a best-fitting method to experimental data. Subsequently, this empirical formula has been applied to the n-type metal oxides of $Zn_{1+x}O$, $Cd_{1+x}O$, and $PrO_{1.8003-x}$, and the p-type metal oxides of CoO_{1+x}, FeO_{1+x}, and Cu_2O_{1+x}. It gives a very good agreement with the experimental data through the best-fitted parameters within 6% of relative error. It is also possible to explain approximately qualitative characters of the parameters A,B,C,D and a,b,c,d from theoretical bases.

Introduction

Since Wagner and Schottky[1] had shown that inorganic compounds could have defects in crystals and nonstoichiometric compositions, experimental and theoretical studies for these behaviors have been performed actively.[2-19] Among these, the enthalpy and entropy changes of point defect formations in metal oxides were usually determined by the deviation from stoichiometry, electrical conductivities, and diffusions as a function of temperature or partial pressures of oxygen. In this respect, compositional variations in many nonstoichiometric oxides are often discussed as a function of temperature or partial pressure of oxygen[7-11,20,21] and approximate empirical relations between these have been proposed.[22-26]

Usually the relationships between nonstoichiometric quantity, log x and inverse temperature (1000/T) or oxygen partial pressure ($\log P_{O_2}$) have been considered to be linear. The linear relationship is based on the fact that the defects are randomly distributed and noninteracting to each other with mass action law. This is probably true only in the range of very small deviations from stoichiometry. Consequently, in many cases, to fit experimental data, one has to adopt two linear relationships[7-11] with so called a break point even though there is no apparent phase transition. Moreover, the slopes of lines in experimental data changes gradually with increasing or decreasing nonstoichiometry. From these facts, it seems that the relationship of real defect system is well represented by curvature rather than linear.

In the present work a new empirical formula is proposed with four parameters which can represent the real defect system. The formula would give a curvature rather than a straight line and would show a consistent result for metal oxides. Characters of parameters A,B,C,D and a,b,c,d obtained from calculations are attempted to be explained qualitatively. The enthalpy of formation of nonstoichiometric composition, $\Delta H'_f$ and the characteristic number, 1/n' are obtained from the new formula.

Empirical Formulas and Calculation

The previous relationships between nonstoichiometric quantity and temperature or oxygen partial pressure were derived theoretically. The usual relationships are the Arrhenius-type equation, which is given by;

$$\log x = a + b\cdot 1000/T$$
$$\log x = a' + b'\cdot \log P_{O_2},$$

where both a and a' are constants, b is $-\Delta H_f/2.3R$, b' is 1/n.

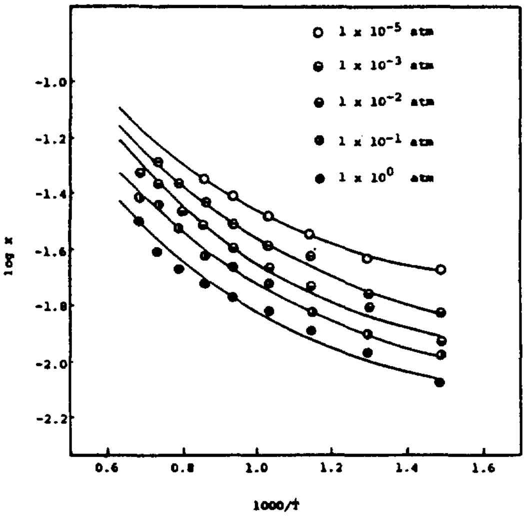

Figure 1. Log x vs. 1000/T for $Zn_{1+x}O$.

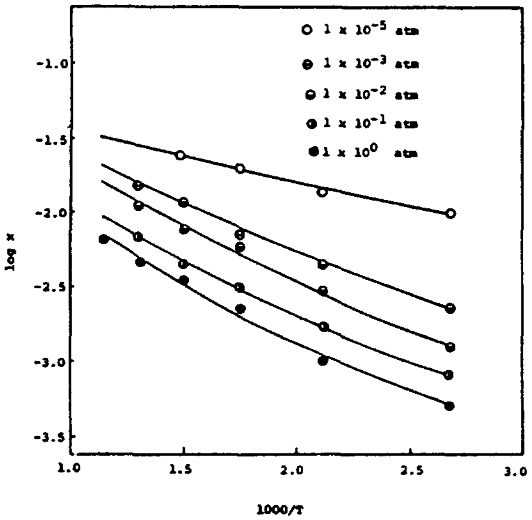

Figure 2. Log x vs. 1000/T for $Cd_{1+x}O$.

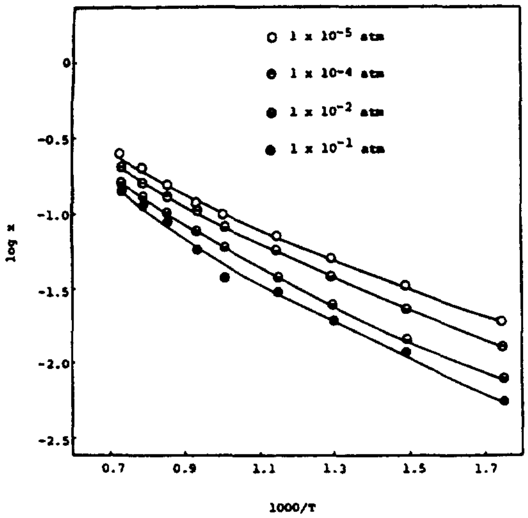

Figure 3. Log x vs. 1000/T for $PrO_{1.8003-x}$.

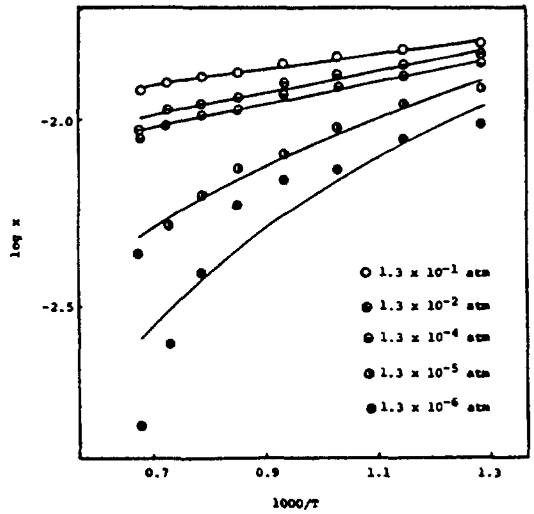

Figure 4. Log x vs. 1000/T for CoO_{1+x}.

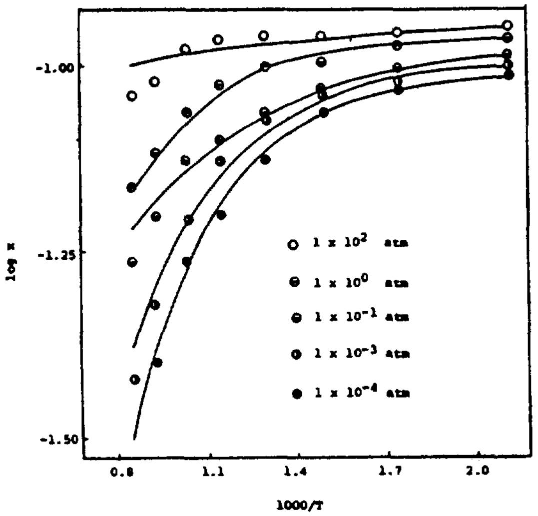

Figure 5. Log x vs. 1000/T for FeO_{1+x}.

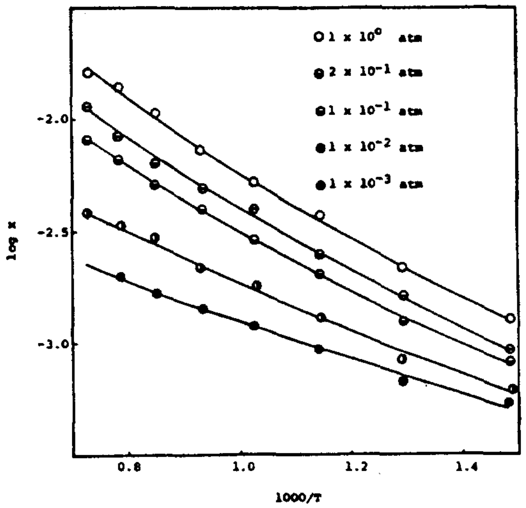

Figure 6. Log x vs. 1000/T for Cu_2O_{1+x}.

Here, ΔH_f is the enthalpy of defect formation and n is a characteristic number identifying the type of defect.

This relation predicts that the values of ΔH_f and 1/n are constants for a temperature and an oxygen partial pressure changes respectively. But experimental data of metal oxides applied to this relation show that these values vary continuously with them. And it is difficult to explain the break point in oxides without a phase transition. On the basis of these facts, new formula seems to be reasonable as a modification which might give a good representation to experimental data within given range of temperature or pressure in experiment. This study tries to find a new empirical formula which can represent the real defect system without considering a particular factor. The equation is Arrhenius-type equation added to a correction term. The proposed formula is obtained mainly by analysing the paper of Choi-Yo *et al.*[7-11] which was studied consistently in the relatively broad ranges of temperature and oxygen partial pressure.

The proposed empirical formulas with four parameters are

(i) in temperature dependence

$$\log x = A + B\cdot 1000/T + C\cdot \exp(-D\cdot 1000/T) \qquad (1)$$

(ii) in oxygen partial pressure dependence

$$\log x = a + b\cdot \log Po_2 + c\cdot \exp(-d\cdot \log Po_2) \qquad (2)$$

where A,B,C,D and a,b,c,d are parameters.

Calculations to get the values of parameters A,B,C,D and a,b,c,d are performed on the basis of best-fitting method with experimental data for temperature and pressure dependence of nonstoichiometric value x of metal oxides, $Zn_{1+x}O$, $Cd_{1+x}O$, and $PrO_{1.8003-x}$ for n-type and CoO_{1+x}, FeO_{1+x} and Cu_2O_{1+x} for p-type.

Results and Discussion

(a) The Empirical Formula for Temperature Dependence.

The plots of log x vs. 1000/T under various pressures for n-type metal oxides; $Zn_{1+x}O$, $Cd_{1+x}O$, and $PrO_{1.8003-x}$, and p-type metal oxides; CoO_{1+x}, FeO_{1+x}, and Cu_2O_{1+x} obtained as a result of the proposed formula, Eq. (1), are shown in Figure 1-6 in comparison to the experimental data. The values of parameters A,B,C,D are shown in Table 1. The ranges of maximum relative error are 0.7~3.1% for $Zn_{1+x}O$, 1.0~2.3% for $Cd_{1+x}O$, 1.1~5.8% for $PrO_{1.8003-x}$, 1.0~8.4% for CoO_{1+x}, 2.9~7.0% for FeO_{1+x}, and 1.0~2.4% for Cu_2O_{1+x}. These represent a good agreement with experimental data except somewhat large errors in the case of CoO_{1+x} and FeO_{1+x} at low pressures. The break point are vanished from these plots, which was difficult to be explained previously. From the plots of the values of the calculated best-fitted parameters A,B,C,D vs. log Po_2, tendencies of each parameter for n-type and p-type metal oxides can be derived. In both cases, variations of A, B and D show linearities, while variation of C shows exponent. For n-type metal oxides, parameters A and B decrease and parameters C and D increase as pressure increases. Whereas for p-type metal oxides, as pressure increases, parameters A, B, and C increase with a small change, and parameter D decreases roughly in CoO_{1+x} and FeO_{1+x} and increase in Cu_2O_{1+x}. Therefore, it is clear that the distinctive character between n-type and p-type metal oxides depends on parameters A and B, that is, as pressure increases, parameters A and B decrease for n-type metal oxides and increase for p-type metal oxides.

In the Arrhenius-type equation, where the model is that defects are noninteracting and ditributed randomly, the slope $\partial(\log x)/\partial(1000/T)$ is $-\Delta H_f/2.3R$. With this relation, the enthalpies of formation of nonstoichiometric compositions, ΔH_f, are obtained in ideal system. Similarly, we tried to get the enthalpies of formation in the system which should consider interactions between defects. The new proposed formula with the correction term represents experimental data satisfac-

Table 1. The Values of Best-fitted Parameters A,B,C,D for Semiconductive Metal Oxides at Various Oxygen Partial Pressures

Pressure (atm)	n-Type Metal Oxides											
	$Zn_{1+x}O$				$Cd_{1+x}O$				$PrO_{1.8003-x}$			
	A	B	C	D	A	B	C	D	A	B	C	D
1×10^{-5}	-1.55	-0.15	2.26	2.27	-1.54	-0.350	0.46	0.023	-1.20	-0.55	1.69	0.78
1×10^{-4}	-1.60	-0.16	2.38	2.23	-1.80	-0.352	0.57	0.043	-1.30	-0.57	1.86	0.84
1×10^{-3}	-1.65	-0.17	2.82	2.41	-2.04	-0.354	1.28	0.48	-1.40	-0.59	2.32	1.00
1×10^{-2}	-1.70	-0.19	3.29	2.67	-2.24	-0.356	1.82	0.66	-1.50	-0.16	2.31	0.95
1×10^{-1}	-1.75	-0.20	2.83	2.58	-2.35	-0.358	1.81	0.79	-1.60	-0.63	2.48	0.98
1×10^{0}	-1.80	-0.21	3.06	2.84	-2.49	-0.360	2.39	1.00	—	—	—	—

Pressure (mmHg)	p-Type Metal Oxides											
	CoO_{1+x}				FeO_{1+x}				Cu_2O_{1+x}[a]			
1×10^{-4}	—	—	—	—	-1.02	0.007	-9.93	3.55	—	—	—	—
1×10^{-3}	-2.18	0.28	-2.87	2.32	-1.01	0.006	-7.12	3.46	-4.50	-0.30	2.55	0.29
1×10^{-2}	-2.16	0.27	-1.53	2.25	-1.00	0.005	-3.74	3.05	-4.10	-0.32	2.69	0.46
1×10^{-1}	-2.14	0.26	-0.11	0.80	-0.99	0.004	-1.75	2.35	-3.70	-0.34	3.02	0.68
2×10^{-1}	—	—	—	—	—	—	—	—	-3.58	-0.35	3.26	0.76
1×10^{0}	-2.11	0.25	-0.12	0.70	-0.97	0.003	-12.4	4.58	-3.30	-0.36	3.36	0.86
1×10^{1}	-2.09	0.24	-0.17	1.32	-0.96	0.002	-3.49	3.80	—	—	—	—
1×10^{2}	-2.06	0.23	-0.01	-0.11	-0.95	0.001	-0.22	1.61	—	—	—	—

[a] Units of oxygen partial pressures are atm in the case of Cu_2O_{1+x}.

Table 2. Comparisons of Enthalpies of Formation of the Nonstoichiometric Compositions of the Present Formula, $\Delta H'_f$ (kcal/mol) with the Arrhenius Type Equation, ΔH_f (kcal/mol) for Semiconductive Metal Oxides

Pressure (atm)	$Zn_{1+x}O$			$Cd_{1+x}O$		$PrO_{1.8003-x}$		
	$\Delta H'_f$	ΔH_f		$\Delta H'_f$	ΔH_f	$\Delta H'_f$	ΔH_f	
	(900~400°C)			(500~100°C)		(900~300°C)		
1×10^{-5}	5.68~1.49	4.53	2.20	1.65~1.64	1.65	6.06~4.06	5.85	4.26
1×10^{-4}	6.08~1.62	4.58	2.20	1.71	1.83	6.64~4.25	6.20	4.58
1×10^{-3}	6.84~1.66	4.78	2.52	3.13~2.39	2.75	8.07~4.55	6.26	5.23
1×10^{-2}	7.40~1.61	4.98	2.53	3.96~2.56	2.93	8.05~4.67	7.18	5.28
1×10^{-1}	6.69~1.63	5.81	2.53	3.99~2.42	3.02	8.59~4.89	8.36	5.38
1×10^{0}	6.74~1.54	7.28	2.54	4.64~2.39	3.11	—	—	—

Pressure (mmHg)	CoO_{1+x}			FeO_{1+x}		Cu_2O_{1+x}[a]	
	$\Delta H'_f$	ΔH_f		$\Delta H'_f$	ΔH_f	$\Delta H'_f$	ΔH_f
	(1200~500°C)			(900~200°C)		(1000~500°C)	
1×10^{-4}	—	—	—	-14.52~-0.044	—	—	—
1×10^{-3}	-7.56~-2.78	-15.8	-2.06	-10.79~-0.038	—	4.14~3.58	4.58
1×10^{-2}	-4.64~-2.08	-5.95	-2.06	-6.59~-0.037	—	5.52~4.32	5.72
1×10^{-1}	-1.43~-1.33	-2.29	-1.03	-3.83~-0.053	—	7.28~4.98	6.64
2×10^{-1}	—	—	—	—	—	8.07~5.24	7.09
1×10^{0}	-1.37~-1.29	-1.95	-1.03	-2.54~-0.015	—	8.71~5.32	7.32
1×10^{1}	-1.51~-1.28	-1.83	-1.03	-4.61~-0.011	—	—	—
1×10^{2}	-1.05	-1.60	-0.69	-0.54~-0.026	—	—	—

[a] Units of oxygen partial pressures are atm in Cu_2O_{1+x}.

torily, which has a slope of
$-\Delta H'_f = 2.3R\{B - C\cdot D\cdot \exp(-D\cdot 1000/T)\}$.

This $\Delta H'_f$ is considered as the enthalpy of formation of nonstoichiometric compositions which may represent not ideal defect formation but real defect formation. The enthalpies of formation, $\Delta H'_f$, obtained from the present formula are shown in Table 2 for semiconductive metal oxides. The comparison to enthalpies of formation from the Arrhenius-type equation are shown in these tables. All of these enthalpies have certain ranges changing both with temperature and pressure. In temperature dependence, the enthalpies of formation of all n-type metal oxides and Cu_2O_{1+x} of p-type metal oxides increase as temperature increases. In the case of CoO_{1+x} and FeO_{1+x}, the absolute value of enthalpy increase as temperature increases. Especially in FeO_{1+x}, enthalpies could not be found from the Arrhenius-type equation because experimental data represent curvature originally. The variations of enthalpy with temperature correspond qualitatively to the phenomena that the values 1/n obtained by experimental data change gradually with temperature. Under the various pressures, as shown in Table 2, the enthalpies of formation tend to increase as pressure increases in all the n-type metal oxides and Cu_2O_{1+x} of p-type metal oxides. In the case of CoO_{1+x} and FeO_{1+x} of p-type metal oxides, the absolute values of enthalpies decrease as pressure increases.

(b) The Empirical Formula for Oxygen Pressure Dependence

The plots of log x vs. log Po_2 under various temperatures obtained as a result of the proposed formula, Eq.(2), are shown in Figure 7-12 for the same materials as dealt with temperature dependence. All of them show curvature without the break point. The values of parameters a,b,c,d are shown in Table 3. The ranges of maximum relative error are 0.8~5.4% for n-type and p-type metal oxides. These represent a good agreement with the experimental data.

In pressure dependence, tendencies of each parameter, a,b,c,d for n-type and p-type metal oxides show linearity except tendency of c for the p-type. The variation of c for the p-type metal oxides shows exponent. There is no distinctive consistancy between n-type and p-type metal oxides in tendencies of parameters of pressure dependence.

From the Arrhenius-type equation, slope $\partial(\log x)/\partial(\log Po_2)$ is 1/n, where n is a characteristic number identifying the type of defect. Usually the type of defect can be distinguished from n value for a metal oxides. Therefore 1/n′ value is derived with the new proposed formula similarly. From the new proposed formula, slope is as follows;

$$1/n' = b - c\cdot d\cdot \exp(-d\cdot \log Po_2).$$

The characteristic numbers 1/n′ obtained from the present formula are shown in Table 4 for semiconductive metal oxides with the comparison to characteristic numbers 1/n. All of these 1/n′ values have certain ranges changing with pressure and temperature and approximately agree with changing 1/n values which are difficult to be explained by equation log x $\propto$ 1/n log Po_2. Here, 1/n′ values for all n-type metal oxides are negative and those for all p-type metal oxides are positive. This is the well-known ditinctive difference between n-type and p-type metal oxides. Furthermore, knowing the characteristic number n would guide establishing the defect mechanism of a metal oxide. Thus variation of n′ value with changing oxygen partial pressure at a given temperature can be interpreted as relatively gradual change of serveral defect mechanism instead of single mechanism at a given

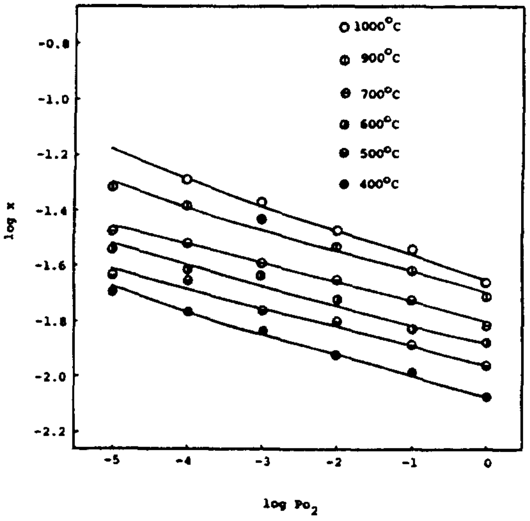

Figure 7. Log x vs. log Po_2 for $Zn_{1+x}O$.

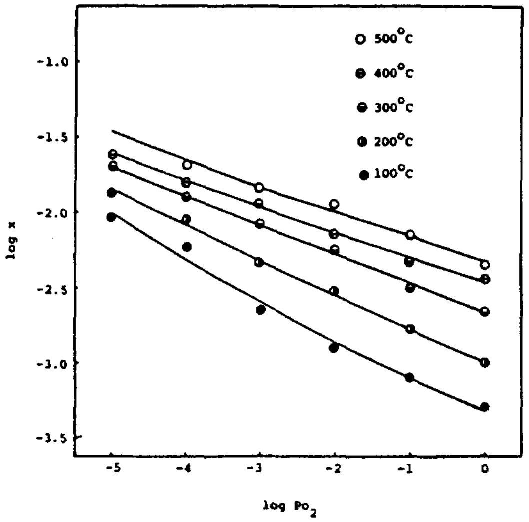

Figure 8. Log x vs. log Po_2 for $Cd_{1+x}O$.

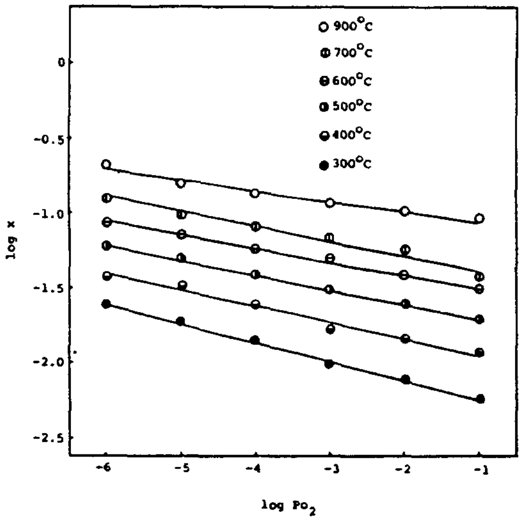

Figure 9. Log x vs. log Po_2 for $PrO_{1.8003-x}$.

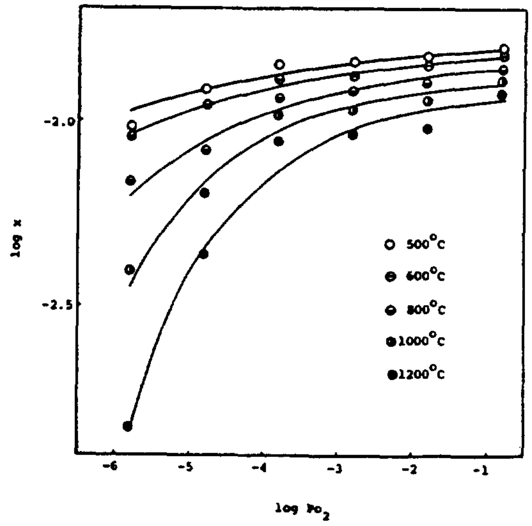

Figure 10. Log x vs. log Po_2 for CoO_{1+x}.

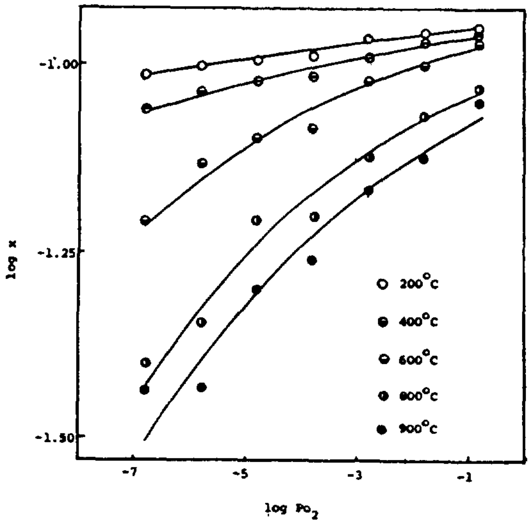

Figure 11. Log x vs. log Po_2 for FeO_{1+x}.

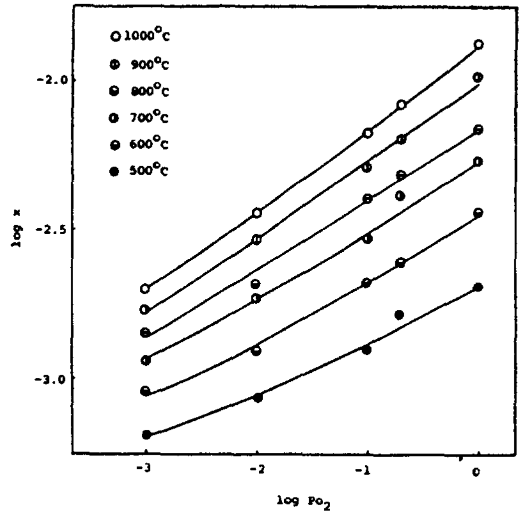

Figure 12. Log x vs. log Po_2 Cu_2O_{1+x}.

Table 3. The Values of Best-fitted Parameters a,b,c,d for Semiconductive Metal Oxides at Various Temperatures

Temperature (°C)	n-Type Metal Oxides											
	$Zn_{1+x}O$				$Cd_{1+x}O$				$PrO_{1.8003-x}$			
	a	b	c	d	a	b	c	d	a	b	c	d
200	—	—	—	—	-3.25	-0.194	0.26	0.10	—	—	—	—
300	—	—	—	—	-3.12	-0.194	0.46	-.003	-2.83	-0.135	0.45	-.015
400	-2.11	-.068	0.034	.021	-3.02	-0.193	0.56	-.048	-2.67	-0.130	0.61	-.040
500	-2.07	-.066	0.11	.021	-2.96	-0.193	0.64	-.054	-2.54	-0.126	0.72	-.040
600	-2.04	-.064	0.16	.029	—	—	—	—	-2.45	-0.123	0.86	-.048
700	-2.02	-.062	0.22	.017	—	—	—	—	-2.37	-0.121	0.90	-.032
800	-2.00	-.061	0.23	.057	—	—	—	—	-2.31	-0.119	1.06	-.056
900	-1.98	-.060	0.28	.056	—	—	—	—	-2.25	-0.117	1.13	-.049

Temperature (°C)	p-Type Metal Oxides											
	CoO_{1+x}				FeO_{1+x}				Cu_2O_{1+x}			
300	—	—	—	—	-0.935	.0112	-.0073	0.18	—	—	—	—
400	—	—	—	—	-0.935	.0115	-.011	0.23	—	—	—	—
500	-1.77	.010	-.016	0.38	-0.935	.0117	-.014	0.31	-3.77	0.374	1.08	0.15
600	-1.80	.011	-.0079	.054	-0.935	.0119	-.022	0.33	-3.71	0.377	1.26	0.11
700	-1.82	.012	-.0061	0.66	-0.935	.0120	-.033	0.31	-3.67	0.379	1.40	.095
800	-1.84	.014	-.0058	0.68	-0.935	.0121	-.069	0.26	-3.64	0.381	1.48	.089
900	-1.86	.014	-.0062	0.70	-0.935	.0122	-.10	0.23	-3.61	0.383	1.60	.069
1000	-1.87	.015	-.0050	0.79	—	—	—	—	-3.58	0.384	1.71	.056
1200	-1.91	.016	-.0047	0.91	—	—	—	—	—	—	—	—

Table 4. Comparisons of the Defect Characteristic Values of the Present Formula, 1/n′ with Experimental Values, 1/n for Semiconductive Metal Oxides

Temperature (°C)	$Zn_{1+x}O$		$Cd_{1+x}O$		$PrO_{1.8003-x}$	
	1/n′ ($10^{-5}\sim10^{0}$ atm)	1/n	1/n′ ($10^{-5}\sim10^{0}$ atm)	1/n	1/n′ ($10^{-6}\sim10^{-1}$ atm)	1/n
200	—	—	-1/4.21∼-1/4.53	-1/4.65	—	—
300	—	—	-1/5.20∼-1/5.21	-1/5.26	-1/7.8	-1/ 7.8
400	-1/14.6	-1/14.0	-1/5.82∼-1/6.03	-1/6.06	-1/ 9.1∼-1/ 9.4	-1/ 8.8
500	-1/14.7	-1/13.8	-1/6.03∼-1/6.35	-1/6.90	-1/ 9.7∼-1/10.2	-1/ 9.7
600	-1/14.5∼-1/14.6	-1/12.8	—	—	-1/10.9∼-1/12.0	-1/10.9
700	-1/15.1∼-1/15.2	-1/12.3	—	—	-1/10.3∼-1/10.8	-1/11.5
800	-1/12.7∼-1/13.5	-1/11.6	—	—	-1/13.1∼-1/16.0	-1/13.0
900	-1/12.4∼-1/13.2	-1/11.1	—	—	-1/13.2∼-1/15.6	-1/17.1

Temperature (°C)	CoO_{1+x}			FeO_{1+x}		Cu_2O_{1+x}	
	1/n′ ($10^{-3}\sim10^{2}$ mmHg)	1/n		1/n′ ($10^{-4}\sim10^{2}$ mmHg)	1/n	1/n′ ($10^{-3}\sim10^{0}$ mmHg)	1/n
300	—	—		1/63.2∼1/78.4	1/40	—	—
400	—	—		1/41.5∼1/68.6		—	—
500	1/14.8∼1/53.7	1/12	1/75	1/20.8∼1/57.4	1/10	1/4.68∼1/8.07	1/5.26
600	1/ 8.9∼1/54.9	1/12		1/12.4∼1/44.6		1/4.28∼1/5.74	1/4.59
700	1/ 4.9∼1/51.1	1/9		1/ 9.8∼1/38.8		1/4.07∼1/4.95	1/4.44
800	1/ 4.5∼1/48.5	1/8.3		1/ 8.1∼1/28.5	—	1/4.00∼1/4.77	1/4.31
900	1/ 3.7∼1/44.9	1/7.4	1/43	1/ 8.0∼1/24.4	—	1/3.67∼1/4.05	1/4.00
1000	1/ 2.3∼1/43.5	1/4.8		—	—	1/3.47∼1/3.70	1/3.64
1200	1/ 1.1∼1/39.3	1/2.8		—	—	—	—

temperature.

Conclusion

From the linear relation by Arrhenius-type equation, n-type metal oxides can be distinguished from p-type metal oxide in that in the former nonstoichiometric quantity tended to decrease as pressure increased and converged in high temperature. Whereas in the latter it tended to increase as pressure increased and converged in low temperature. These distinctive differences between n-type and p-type metal oxides have become more obvious by present equation.

For n-type and p-type metal oxides applied to the proposed formula, temperature and pressure dependences of nonstoichiometric value are expressed as curvature without break point. Clearly, an improvement of the present formula from the Arrhenius-type equation is that increasing nonstoichiometric value as raising temperature can be shown naturally besides removing the break point which is difficult to be explained. Pressure dependence is similar to this, too. Therefore, we may say that an advantage of present formula is that the variation of ΔH_f and $1/n$ values can be explained qualitatively, that is, the real defect formation can be explained.

We expect that the validity of new formula can be found if interactions among defects are considered. It is because the Arrhenius-type equation is derived in ideal system where defects are randomly distributed and noninteracting. In future, the problem is to attempt a theoretical approach considering interactions among defects.

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