

Theoretical estimation of heat capacity, density and thermal expansivity of liquid metal alloys

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Theoretical formulation has been made for estimating heat capacity, density and thermal expansivity of liquid metal alloys of Na+Cs and K+Rb at three different temperatures and at various compositions. The entire formulation has been based on Flory's statistical theory. Theoretically estimated values have been compared with the observed values from literature, and good agreement has been found.

The study of metal alloys is very useful in industry as heat transfer media in the field of nuclear power generation. This interest is stimulated by the need to remove large quantity of heat from nuclear power reactors at moderate coolant velocities and temperature drops. Liquid metal alloys possess many desirable characteristics such as low vapour pressure, high thermal conductivities, high boiling points, thermal and reaction stability which permits low pressure operation of coolant systems at high temperatures and radiation fluxes. The thermodynamic properties of metal alloys are well known as a general rule, but there are temperature regions where accurate information does not exist. The experimental data at elevated temperatures steam from the high chemical reactivity of these substances. They will easily react with components of the surrounding atmosphere such as oxygen, nitrogen, carbon dioxide and water vapour. It is difficult to obtain materials of high purity, and the samples get contaminated easily during measurements. This is true for alkali metal alloys. Hence it is worthwhile to estimate some useful and important properties of metal alloys theoretically. Very recently attempt has been made to apply theoretical approaches for computing density and other properties of multicomponent electrolytic solutions¹ and multicomponent non-electrolytic mixtures² with successful results. In the present work we are formulating a method for the estimation of density and heat capacity of liquid metal alloys containing

alkali metals. The results of theoretical calculations are compared with the experimental findings available in literature^{3,4}.

Formulation

The most widely employed Flory's statistical theory^{5,6} during recent past⁷⁻¹⁶, will be utilized here to estimate the density(ρ) and heat capacity at constant pressure(C_p) of Na+Cs and K+Rb alloys at 323.15 K, 423.15 K and 523.15 K. For liquid metal alloys (two component), the Flory parameters are given by

$$P_{Alloy}^* = \left[(\Psi_1 P_1^* + \Psi_2 P_2^*) - (\Psi_1 \theta_2 X_{Alloy}) \right] \quad \dots(1)$$

where P_{Alloy}^* , X_{Alloy} , P_1^* and P_2^* are respectively the characteristic pressure of alloy, interaction parameter of alloy, characteristic pressure of pure metals (1 and 2) constituting the alloy, Ψ_1 and Ψ_2 are the respective segment fractions of pure metals 1 and 2, θ_2 being the site fraction of 2, X_{Alloy} and T_{Alloy}^* are given by

$$X_{Alloy} = P_1^* \left[1 - \left(\frac{P_2^*}{P_1^*} \right)^{1/2} \left(\frac{V_2^*}{V_1^*} \right)^{1/6} \right] \quad \dots(2)$$

$$T_{Alloy}^* = \frac{P_{Alloy}^*}{\left(\frac{\Psi_1 P_1^*}{T_1^*} + \frac{\Psi_2 P_2^*}{T_2^*} \right)} \quad \dots(3)$$

V_1^* , V_2^* and T_1^* , T_2^* are respectively the characteristic volumes and temperatures of pure metals 1 and 2. The reduced temperature ($\tilde{T}_{Alloy}$), ideal reduced volume ($\tilde{V}_{Alloy}^\circ$) and ideal reduced temperature ($\tilde{T}_{Alloy}^\circ$) of alloy can be expressed as

$$\tilde{T}_{Alloy} = \frac{T}{T_{Alloy}^*} \quad \dots(4)$$

$$\tilde{V}_{Alloy}^\circ = x_1 \tilde{V}_1 + x_2 \tilde{V}_2 \quad \dots(5)$$

$$\tilde{T}_{Alloy}^\circ = \frac{(\tilde{V}_{Alloy}^\circ)^{1/3} - 1}{(\tilde{V}_{Alloy}^\circ)^{4/3}} \quad \dots(6)$$

The excess volume (V_{Alloy}^E), reduced volume ($\tilde{V}_{Alloy}$), characteristic volume (V_{Alloy}^*) and molar volume (V_{Alloy}) of alloy are related by the expressions

$$V_{Alloy}^E = (x_1 V_1 + x_2 V_2) \tilde{V}_{Alloy}^E \quad \dots(7)$$

$$\tilde{V}_{Alloy}^E = \tilde{V}_{Alloy}^{\circ 7/3} \left(\frac{4}{3} - \tilde{V}_{Alloy}^{\circ 1/3} \right) (\tilde{T}_{Alloy} - \tilde{T}_{Alloy}^\circ) \quad \dots(8)$$

$$\tilde{V}_{Alloy} = \tilde{V}_{Alloy}^E + \tilde{V}_{Alloy}^\circ \quad \dots(9)$$

$$V_{Alloy}^* = \frac{V_{Alloy}}{\tilde{V}_{Alloy}} \quad \dots(10)$$

The heat capacity, $(C_p)_{Alloy}$, excess heat capacity, $(C_p^E)_{Alloy}$ and $(C_p)_{idl}$ of alloy are obtained from the following relations¹⁰:

$$(C_p)_{Alloy} = (C_p^E)_{Alloy} + (C_p)_{idl} \quad \dots(11)$$

$$(C_p^E)_{Alloy} = \frac{P_{Alloy}^* V_{Alloy}^*}{T_{Alloy}^*} \left[\frac{1}{\left(\frac{4}{3} \tilde{V}_{Alloy}^{1/3} - 1 \right)} - \sum_i \left\{ \frac{x_i}{\left(\frac{4}{3} \tilde{V}_i^{1/3} \right)} \right\} \right] \quad \dots(12)$$

$$(C_p)_{idl} = \sum x_i C_{p,i} \quad \dots(13)$$

where $C_{p,i}$ is the heat capacity of respective pure metals.

For the estimation of density, ρ_{Alloy} , of alloy, following simple expression is employed:

$$\rho_{Alloy} = \frac{M_{Alloy}}{V_{Alloy}} \quad \dots(14)$$

where M_{Alloy} and V_{Alloy} are respectively the molar mass and molar volume of alloy. This expression can be converted in terms of mole fractions x_1 and x_2 of metal components, and reduced volume, $\tilde{V}_{Alloy}$, of alloy using Eqs (7) to (10),

$$\rho_{Alloy} = \frac{x_1 M_1 + x_2 M_2}{(x_1 V_1^* + x_2 V_2^*) \tilde{V}_{Alloy}} \quad \dots(15)$$

Thermal expansion coefficient, α_{Alloy} , of the alloy is obtained from the following expression¹²

$$\alpha_{Alloy} = \frac{3(\tilde{V}_{Alloy}^{1/3} - 1)}{T[1 - 3(\tilde{V}_{Alloy}^{1/3} - 1)]} \quad \dots(16)$$

Results and Discussion

The heat capacity at constant pressure, $(C_p)_{Alloy}$, and the density ρ_{Alloy} , of Na+Cs and K+Rb alloy are calculated at three different temperatures viz. 323.15, 423.15 and 523.15 K. Ultrasonic absorption, velocity and density of these metal alloys were very accurately determined by Kim and Letcher^{3,4} at above temperatures and varying compositions of alloys. For the calculation of $(C_p)_{Alloy}$, we have employed Eqs (11), (12) and (13) whereas for density computation, Eqs (14) and (15) were used. In these cases, we require the values of characteristic and reduced parameters of alloy and their constituents metals at desired temperatures. These are estimated from Eqs (1) to (10). Calculated values of $(C_p)_{Alloy}$, and ρ_{Alloy} , for the two liquid metal alloys at 323.15, 423.15 and 523.15 K as a function of composition are recorded in Table 1. For a comparative study, the experimental values, reported by Kim and Letcher, are also included in Table 1. Similarly the values of thermal expansivity (α_{Alloy}) of the alloys have been calculated from Eq. (16). These values are also included in Table 1.

Table 1 — Calculated values of $(C_p)_{\text{Alloy}}$, ρ_{Alloy} , α_{Alloy} and their percentage deviation (Δ) for Na+Cs & K+Rb Alloy

Na+Cs	(C _p) _{Alloy}		Δ%	ρ _{Alloy}		Δ%	α _{Alloy}		Δ%
	Theo	Expt		Theo	Expt		Theo	Expt	
T=323.15K									
x _{Na}									
0.197	338.06	338.10	0.01	1.3664	1.3660	-0.03	2.716	2.716	0.01
0.340	335.34	335.40	0.02	1.2837	1.2840	0.03	2.705	2.705	0.01
0.510	332.11	332.10	0.00	1.1789	1.1790	0.01	2.691	2.692	0.04
0.594	330.51	330.05	-0.14	1.1243	1.1240	-0.03	2.684	2.685	0.05
0.710	328.31	328.30	0.00	1.0456	1.0460	0.03	2.673	2.674	0.02
0.821	326.20	326.20	0.00	0.9666	0.9670	0.04	2.663	2.664	0.03
0.862	325.42	325.40	-0.01	0.9364	0.9370	0.07	2.659	2.660	0.02
0.950	323.75	323.70	-0.02	0.8696	0.8690	-0.07	2.651	2.651	0.00
T=423.15K									
0.197	322.86	322.80	-0.02	1.3288	1.3290	0.01	2.861	2.862	0.04
0.340	321.01	321.00	0.00	1.2485	1.2490	0.04	2.848	2.849	0.03
0.510	318.82	318.00	-0.01	1.1468	1.1460	-0.07	2.833	2.834	0.05
0.594	317.74	317.70	-0.01	1.0938	1.0940	0.02	2.825	2.826	0.05
0.710	316.24	316.20	-0.01	1.0174	1.0180	0.06	2.813	2.814	0.04
0.821	314.81	314.80	0.00	0.9406	0.9410	0.04	2.802	2.803	0.05
0.862	314.28	314.30	0.01	0.9112	0.9110	-0.03	2.797	2.798	0.03
0.950	313.14	313.10	-0.01	0.8464	0.8460	-0.04	2.788	2.788	0.01
T=523.15K									
0.197	310.46	310.50	0.01	1.2904	1.2900	-0.03	3.013	3.014	0.02
0.340	309.43	309.40	-0.01	1.2111	1.2130	0.16	3.032	3.001	-1.02
0.510	308.18	308.20	0.01	1.1139	1.1140	0.00	2.981	2.983	0.06
0.594	307.57	307.60	0.01	1.0626	1.0620	-0.05	2.972	2.974	0.06
0.710	306.72	306.70	-0.01	0.9885	0.9890	0.05	2.959	2.961	0.07
0.821	305.91	305.90	0.00	0.9140	0.9140	0.01	2.946	2.947	0.04
0.862	305.61	305.60	0.00	0.8855	0.8860	0.06	2.941	2.942	0.03
0.950	304.97	305.00	0.01	0.8225	0.8220	-0.06	2.930	2.931	0.03

(Contd.)

Table 1 — Calculated values of $(C_p)_{\text{Alloy}}$, ρ_{Alloy} , α_{Alloy} and their percentage deviation (Δ) for Na+Cs & K+Rb alloy — *Contd*

K+Rb	(C _p) _{Alloy}		Δ%	ρ _{Alloy}		Δ%	α _{Alloy}		Δ%
	Theo	Expt		Theo	Expt		Theo	Expt	
T = 323.15K									
x _K									
0.223	347.29	347.00	-0.08	1.7642	1.7500	-0.81	2.483	2.790	11.01
0.623	335.33	335.00	-0.10	1.5076	1.5100	0.16	2.704	2.650	-2.03
0.723	332.34	333.00	0.02	1.4059	1.4300	1.69	2.744	2.600	-5.54
0.765	331.08	331.00	-0.03	1.3554	1.3600	0.33	2.758	2.560	-7.74
0.870	327.94	328.00	0.02	1.2016	1.2100	0.70	2.784	2.470	-12.71
0.907	326.84	326.00	-0.26	1.1350	1.1400	0.44	2.789	2.430	-14.79
0.927	326.24	326.00	-0.07	1.0956	1.1100	1.30	2.791	2.410	-15.82
0.946	325.67	325.00	-0.21	1.0556	1.0700	1.34	2.793	2.390	-16.85
0.958	325.31	325.00	-0.10	1.0290	1.0400	1.06	2.793	2.370	-17.85
0.981	324.62	324.00	-0.19	0.9747	0.9900	1.54	2.793	2.340	-19.37
T = 423.15K									
0.223	331.45	331.00	-0.13	1.7023	1.7000	-0.14	2.892	2.910	0.61
0.623	321.45	321.00	-0.14	1.4720	1.4700	-0.13	2.725	2.770	1.64
0.723	318.94	319.00	0.02	1.3771	1.4000	1.64	2.664	2.730	2.40
0.765	317.89	318.00	0.03	1.3295	1.3300	0.04	2.636	2.680	1.63
0.870	315.26	315.00	-0.08	1.1827	1.1800	-0.23	2.557	2.600	1.64
0.907	314.33	314.00	-0.11	1.1186	1.1200	0.12	2.526	2.560	1.31
0.927	313.83	314.00	0.05	1.0805	1.0800	-0.05	2.506	2.530	0.83
0.946	313.35	313.00	-0.11	1.0418	1.0400	-0.18	2.492	2.510	0.73
0.958	313.05	313.00	0.02	1.0160	1.0100	-0.60	2.481	2.490	0.38
0.981	312.48	313.00	0.17	0.9632	0.9600	-0.33	2.459	2.460	0.06
T = 523.15K									
0.223	317.78	318.00	0.07	1.6508	1.6500	-0.05	3.016	3.060	1.45
0.623	310.19	310.00	-0.06	1.4283	1.4300	0.12	2.863	3.020	5.21
0.723	308.29	308.00	-0.09	1.3368	1.3600	1.17	2.803	2.880	2.67
0.765	307.49	307.00	-0.16	1.2909	1.2900	-0.07	2.775	2.840	2.30
0.870	305.48	305.00	-0.16	1.1492	1.1500	0.07	2.694	2.800	3.80
0.907	304.78	304.00	-0.26	1.0873	1.0900	0.25	2.661	2.720	2.16
0.927	304.40	304.00	-0.13	1.0504	1.0500	-0.04	2.643	2.680	1.38
0.946	304.03	304.00	-0.01	1.0130	1.0100	-0.03	2.625	2.660	1.32
0.958	303.80	303.00	0.27	0.9880	0.9900	0.20	2.613	2.640	1.02
0.981	303.36	303.00	-0.12	0.9369	0.9400	0.33	2.590	2.630	1.52

A close inspection of Table 1 shows that the theoretically calculated values of heat capacity at constant pressure and density of Na+Cs and K+Rb alloys decrease with an increase in temperature and as well as the mole fraction of component first. The agreement between theoretically, calculated values and experimental findings^{3,4} is quite good. The trend in the variation of theoretically calculated values of both heat capacity at constant pressure and density with temperature and composition is found to be the same as observed experimentally for both the alloys.

The thermal expansivity values, calculated theoretically for Na+Cs and K+Rb liquid metal alloys, increase with an increase in temperature and the mole fraction of the first component following the trend similar to the observed data. The agreement between theoretically calculated values and experimental values is quite satisfactory. The deviation in the calculated values of thermal expansivity at 323.15 K in the case of K+Rb alloy may be due to the approximations used in the theoretical formalism. Also, thermal expansivity is very sensitive to the temperature and composition. On the whole the agreement is quite reasonable.

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