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Thermodynamic Study of Lithium–Vanadium Bronzes by Coulometric Titration

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Thermodynamic study has been made of lithium–vanadium bronzes β-$Li_xV_2O_{5-y}$ in reversible cells with a lithium-conducting solid electrolyte using coulometric titration. The linear dependence of $\Delta\bar{G}_{Li}$ in the bronze on parameters x and T was found. It is concluded that the dependence of $\Delta\bar{G}_{Li}$ on the P_{O_2} value is weak. The limits of the homogeneity region of β-$Li_xV_2O_{5-y}$ have been more clearly defined.

Introduction

In recent years, studies on reversible current sources, using alkali metals as the anode, have become more intensive. Of particular interest, owing to the high voltage and specific energy output, are systems based on lithium compounds (*1*). Work in this direction involves development of new solid electrolytes with high cationic conduction and selection of new electrode materials. The latter should meet a number of requirements (*2*) of which the most important are as follows:

(1) high electronic conduction;
(2) high alkali metal ion mobility;
(3) low activity of the alkali (cathode); and
(4) insignificant variations in the alkali metal activity as a function of composition.

From this viewpoint, the most promising materials are compounds of transition metals, particularly compounds belonging to the class of bronzes (*3*).

In the present work, a thermodynamic study has been made of a bronze of the $Li_xV_2O_{5-y}$ type with a β-phase structure (monoclinic, space group A^2/m, structure group β-$Na_{0.33}V_2O_5$) featuring the highest lithium ion conduction among lithium–vanadium bronzes.

A single-phase sample of β-$Li_xV_2O_{5-y}$ which is in equilibrium with the gas phase represents a three-component system having three ($f=3-2+2=3$) degrees of freedom. The state of this system is characterized by a number of parameters, including T, x, y, P_{O_2}, and $\Delta\bar{G}_{Li}$ (where $\Delta\bar{G}_{Li}$ is the relative partial molar free energy of lithium in the bronze). Only three of the above parameters are independent, the rest being their functions. In a practical study, it is most convenient to select T, x, and P_{O_2} as the independent parameters, since these variables are easier to manipulate and set at a required level. In this case, the thermodynamic study of β-$Li_xV_2O_{5-y}$ includes finding y and $\Delta\bar{G}_{Li}$ as the following functions:

$$y=F_1(x, T, P_{O_2}), \quad (1)$$

$$\Delta\bar{G}_{Li}=F_2(x, T, P_{O_2}). \quad (2)$$

The aim of the present work is to define function (2) using the method of coulometric

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titration in reversible cells with a lithium-conducting solid electrolyte. Used as the latter, in the present study, was β-spodumene $LiAlSi_2O_6$, whose electric properties have been studied in the work discussed in Ref. (*4*).

Experimental

To synthesize the $Li_{0.26}V_2O_5$ bronze, a mixture of vanadium pentoxide and lithium carbonate, prepared in accordance with reaction

$$0.13Li_2CO_3 + V_2O_5 \rightarrow Li_{0.26}V_2O_{5-y} + 0.13CO_2\uparrow + \frac{0.13+y}{2}O_2\uparrow, \qquad (3)$$

was mechanically homogenized under an acetone layer. The dried powder was compressed into pellets 6 mm in diameter and 1 to 3 mm thick, at a pressure of 500 kG/cm^2. The pellets were sintered at 560 to 570°C for 4 hr under a nitrogen flow.

The composition of the $Li_{0.26}V_2O_{5-y}$ bronze used in the thermodynamic study was determined by chemical analysis. A weighed amount of the bronze was dissolved in 20% H_2SO_4 while heating in sealed ampoules without oxygen. The V^{IV} content was found by titration of a sample with a $KMnO_4$ solution; then, the total vanadium content was found in the same sample by titration with a Mohr salt solution. The determination of the lithium content was carried out by the method of atomic absorption.

The composition of the bronze $Li_xV_2O_{5-y}$ may be expressed as $x/2Li_2O \cdot (1-z)V_2^VO_5 \cdot zV_2^{IV}O_4$. The results of chemical analysis allowed one to find the oxygen content in the sample since $y = z - x:2$.

The phase composition of the samples was determined by the powder method on a URS-50 IM diffractometer, using $Fe_{K\alpha}$-irradiation.

The composition of the synthesized bronze is expressed, in accordance with the chemical and X-ray phase analysis data, by the formula β-$Li_{0.262}V_2O_{4.85}$, which agrees with the published data on the existence of the homogeneity region with respect to the oxygen of β-$Li_xV_2O_{5-y}$ $(0 \leq y \leq 0.2\ (5))$. As the y value is a function of state parameters, a coefficient of $5-y$, not 4.85, will be used in this paper.

The β-spodumene $LiAlSi_2O_6$ used as the solid electrolyte was prepared by a ceramic technique from Li_2CO_3, SiO_2, and Al_2O_3 according to the reaction:

$$Li_2CO_3 + Al_2O_3 + 4SiO_2 \rightarrow 2LiAlSi_2O_6 + CO_2\uparrow. \qquad (4)$$

The homogenized mixture of the starting reagents was ground and heated at 1200°K for 2 hr. Then, the powder was ground again and compressed into pellets 6 mm in diameter and 1 mm thick at a pressure of 4000 kG/cm^2. The pellets were sintered in a powder of the same composition at 1570°K for 30 min.

The predominance of Li ionic conductivity in β-spodumene $(t_{Li^+} > 0.99)$ was investigated in the working range of the temperatures (713 to 833°K) and oxygen partial pressures (10^{-4} to $10^{-6.3}$ atm) by dc conductivity measurements in electrochemical cells (A) and (B):

$$Pt|LiAlSi_2O_6|Pt; \qquad (A)$$

$$Pt, Li_{0.26}V_2O_{5-y}|LiAlSi_2O_6|Li_{0.26}V_2O_{5-y}, Pt. \qquad (B)$$

The values of electronic (σ_e) and general $(\sigma_e + \sigma_{Li})$ conductivity of β-spodumene were determined by measuring on direct current the resistance of cells (A) and (B), respectively.

The galvanic cells (A) and (B) as well as (C), (D), and (F) (see further) were constructed from pellets as usual. For example, the design of cell (D) is shown in Fig. 1; the others were constructed in the same way. The surface of the pellets was carefully polished to improve the contact. The weight

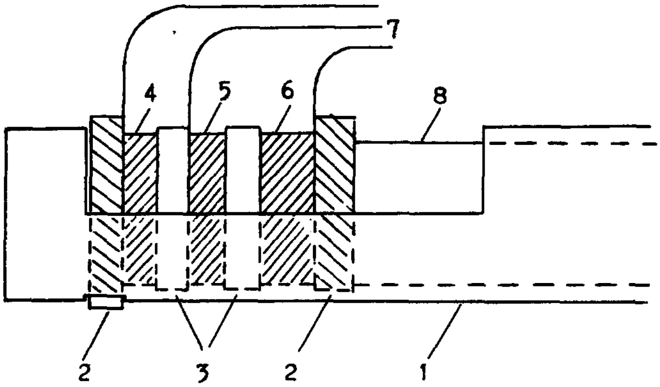


FIG. 1. Galvanic cell (D) for coulometric titration. (1) Alundum cell casing; (2) alundum plates; (3) pellets of solid electrolyte $LiAlSi_2O_6$; (4) reference electrode; (5) working electrode; (6) lithium source; (7) platinum leads; (8) alundum rod.

of pellets was measured (if necessary) on an analytical balance to an accuracy of 0.1 mg.

The controlled value of partial oxygen pressure in a gas phase over the galvanic cells was set by the oxygen buffer which was an equilibrium CuO–Cu_2O mixture maintained at a constant temperature (850 to 1070°K). The scheme of the experimental design is shown in Fig. 2. The CuO–Cu_2O mixture (1) in the form of 3- to 5-mm grains was placed in a quartz tube on a sealed-in quartz mesh. A ZrO_2 (CaO) solid electrolyte cell (2) was used for measuring the oxygen partial pressure in the circulating gaseous mixture. The temperature of the galvanic cell (3) as well as that of cell (2) and oxygen buffer (1) was measured by Pt/Pt–Rh thermocouples. (The latter are not represented.) The change of P_{O_2} in the system was reached (if necessary) by increasing and decreasing the temperature of oxygen buffer (1).

A vacuum pump was joined to the system via a trap (4) cooled by liquid nitrogen. The degree of evacuation in the system was measured using a manometric tube (5). The system was filled with gaseous nitrogen or carbon dioxide through a vacuum cock (6). The gas circulation in the system was realized by a pump consisting of a set of valves (7), a piston (8), and an electromagnetic coil (9).

After the system had been assembled, the vacuum pump was put into action and the cell (3) was heated to 600°K to remove possible organic impurities. Then, after a vacuum of 10^{-3} mm Hg was reached, the system was flushed two or three times and filled with nitrogen or carbon dioxide to a pressure of 1 atm.

The CuO–Cu_2O buffer and the ZrO_2(CaO) cell were heated to the working temperatures of 850 and 1000°K, respectively. The circulation pump was started up and, after a P_{O_2} value lower than 10^{-4} atm was attained in the system, the galvanic cell (3) was heated to a working temperature.

By means of the described design the emfs of the galvanic cells versus temperature (713 to 833°K) and P_{O_2} (10^{-4} to $10^{-6.3}$ atm) were studied. In addition, the emf of galvanic cell (D) was measured as a function of the working electrode composition parameter (x), which was varied in the range of 0.20 to 0.49 by coulometric titration. To this end, a current of a definite value (0.05 to 0.1 mA) was passed through a titration circuit of cell (D). A change of the working electrode composition took place due to the electrochemical transfer of lithium ions through the solid electrolyte. After passing a certain amount of

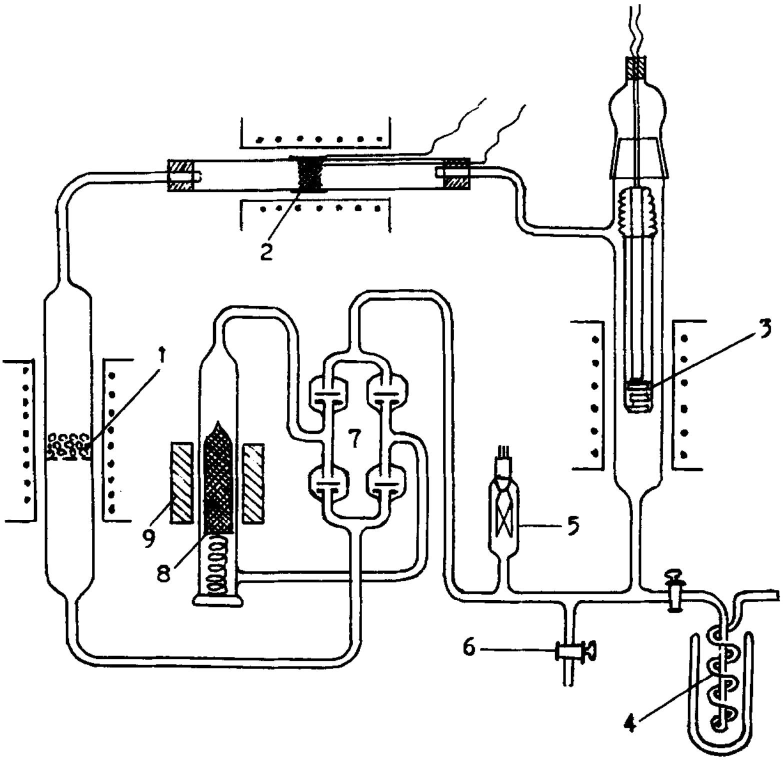


FIG. 2. Experimental set with controlled oxygen partial pressure (see text).

electricity, the current was interrupted and, after an equilibrium emf value was established (from 2 to 4 hr), the dependence of the emf on temperature and P_{O_2} was determined. The criterion of equilibrium was steady emf values within ±0.2 mV for 2 hr at a constant temperature.

The emf data were obtained at both increasing and decreasing state parameters x, T, and P_{O_2} (in discrete steps). No hysteresis was observed. The reproduction of results was better than ±2 mV in cell (C) and ±0.5 mV in cells (D) and (F).

The experimental dependence of emf on state parameters tended to be linear and was processed using the least-squares method as linear relations $E = A + BT$, $E = A_1 + B_1 \lg P_{O_2}$, and $E = A_2 + B_2x$. The errors were assessed relative to the confidence probability interval of 95%.

Results and Discussion

The electrical measurements carried out in electrochemical cells (A) and (B) allowed β-spodumene to be used as a solid electrolyte in our experiments. It was found that in the studied range of T and P_{O_2} the electronic conductivity (σ_e) does not exceed 1×10^{-7} ohm^{-1} cm^{-1} and general conductivity ($\sigma_{Li} + \sigma_e$) in ohm^{-1} cm^{-1} is more than 1.6×10^{-5} at 713°K and 1.2×10^{-4} at 833°K. These results are in a good agreement with published data (*4*): 2.0×10^{-5} and 1.6×10^{-4} ohm^{-1} cm^{-1}, respectively. Therefore in the range of T and P_{O_2} mentioned, β-spodumene satisfies the requirement $t_{Li^+} > 0.99$. This is to be expected since the cations of nontransition elements (Li, Al, Si) do not tend to alter oxidation numbers in the range of T and P_{O_2} used.

Before discussing the emf results, it may be noted that the thermodynamic study of $Li_xV_2O_{5-y}$ bronzes can be carried out by measuring the emf of a galvanic cell:

$$Li_{met}|Li^+|Li_xV_2O_{5-y}.$$

However, we dropped this cell because of the necessity of creating a divided gas space to prevent lithium from oxidation at the P_{O_2} of the existing β-$Li_xV_2O_{5-y}$ phase. Therefore it was necessary to find a reference electrode which is thermodynamically stable in the range of T and P_{O_2} chosen for the experiments. From our point of view the most suitable as such is any composition of the bronze β-$Li_xV_2O_{5-y}$ itself, if its lithium chemical potential is known. We chose the bronze $Li_{0.26}V_2O_{5-y}$ and determined its relative molar free energy of lithium against lithium carbonate, Li_2CO_3, which has a fixed chemical potential of lithium if P_{O_2} and P_{CO_2} in the gas phase are simultaneously fixed. We consider a noticeable lithium ionic conductivity of Li_2CO_3 (*6*) to be favorable for a rapid equilibration in this electrode.

So using Li_2CO_3 as the reference electrode in the cell

$$\begin{array}{l} \text{Pt}, Li_2CO_3|Li^+|Li_{0.26}V_2O_{5-y}, \text{Pt} \\ P_{O_2} = 10^{-4}\text{–}10^{-6.3} \text{ atm} \\ P_{CO_2} = 1 \text{ atm} \end{array} \qquad \text{(C)}$$

the relative partial molar free energy of lithium in the β-$Li_{0.26}V_2O_{5-y}$ bronze was measured.

The emf of galvanic cell (C) is due to the electrochemical reaction

$$\tfrac{1}{2}Li_2CO_3 \rightarrow Li_{(Li_{0.26}V_2O_{5-y})} + \tfrac{1}{2}CO_2 + \tfrac{1}{4}O_2 \qquad (5)$$

We found that the dependence of emf of galvanic cell (C) on oxygen partial pressure is expressed by:

$$E = 660(\pm 20) - 42(\pm 3) \lg P_{O_2}\ (mV)$$
$$(T = 833°\text{K}, P_{O_2} = 10^{-4} \text{ to } 10^{-6.3} \text{ atm}). \qquad (6)$$

Therefore,

$$\Delta G_{(5)} = -63\,700(\pm 2000) + 4050(\pm 300) \lg P_{O_2} \quad \text{(J/mole of lithium)}. \qquad (7)$$

Equation (7) proves the value of $\Delta G_{(5)}$ for keeping a negative sign in the entire P_{O_2} range investigated. This affirmation will be seen further to be correct in all temperature ranges used. A great absolute value of $\Delta G_{(5)}$ and its sign confirms the impossibility of reaction (5) flowing in the reverse direction, i.e., the decomposition of the bronze under CO_2 and O_2 simultaneous action is thermodynamically impossible in our experiments. This note is essential as galvanic cell (C) does not have a divided gas space and the bronze is in the CO_2 atmosphere.

To estimate $\Delta\bar{G}_{Li} = f(P_{O_2})_{T=\text{const}}$ from Eq. (7), it is necessary to take into account that the value of oxygen partial pressure has a bearing upon the chemical potential of lithium in Li_2CO_3. The last value is directly related to the ΔG of the reaction

$$Li_{met} + \tfrac{1}{2}CO_2 + \tfrac{1}{4}O_2 \rightarrow \tfrac{1}{2}Li_2CO_3, \qquad (8)$$

$$\Delta G_{(8)} = \Delta G°_{(8)} + RT \ln(P_{O_2}^{-1/4} \cdot P_{CO_2}^{-1/2}). \qquad (9)$$

The $\Delta G°_{(8)}$ value was calculated as:

$$\Delta G°_{(8)} = -409\,000 + 139T \quad \text{(J/mole of lithium)} \qquad (10)$$

from the thermodynamic data published for Li_2CO_3 and CO_2 (*7*).

The relative partial molar free energy $\Delta\bar{G}_{Li}$ was obtained from substituting (10) into (9) and summarizing reactions (5) and (8) along with their ΔG values:

$$Li_{met} \rightarrow Li_{(Li_{0.26}V_2O_{5-y})} \qquad (11)$$

$$\Delta\bar{G}_{Li} = -356\,000(\pm 2000) + 50(\pm 300) \lg P_{O_2}$$
$$\text{(J/mole)} \quad (T = 833°\text{K}, P_{CO_2} = 1 \text{ atm}). \qquad (12)$$

Equation (12) shows that the dependence of the $\Delta\bar{G}_{Li}$ value on P_{O_2} is weak and cannot be delineated because of experimental error and the small range of P_{O_2} covered. In other words, the error in the $\Delta\bar{G}_{Li}$ determination is greater than the influence of P_{O_2} changes. But this statement is not correct for $\Delta G_{(5)}$ values (compare the coefficients at $\lg P_{O_2}$ in Eqs. (7) and (12)). We shall assume further that $\Delta\bar{G}_{Li}$ in the bronze β-$Li_{0.26}V_2O_{5-y}$ does not depend on P_{O_2}, remembering that it is correct within the experimental error only.

The temperature dependence of the emf of cell (C) is expressed as follows ($P_{O_2} = 10^{-6.3}$ atm, $P_{CO_2} = 1$ atm):

$$E = -622(\pm 10) + 1.86(\pm 0.04)T \quad \text{(mV)}, \tag{13}$$

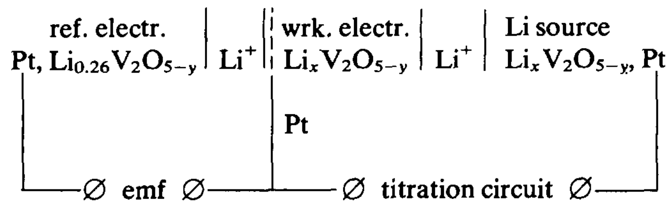
and the free energy of the corresponding reaction (5) is expressed by

$$\Delta G_{(5)} = 60\,000(\pm 1000) - 179(\pm 4)T \quad \text{(J/mole of lithium)}. \tag{14}$$

Comparison of (14) with (9) and (10) gives

$$\Delta\bar{G}_{Li} = -349\,000(\pm 4000) - 10(\pm 4)T \quad \text{(J/mole)} \quad (T = 713 \text{ to } 833\text{°K}). \tag{15}$$

With the value of $\Delta\bar{G}_{Li}$ in the bronze $Li_{0.26}V_2O_{5-y}$ known, one can use this bronze as the reference electrode for the determination of $\Delta\bar{G}_{Li}$ in the whole region of homogeneity of β-$Li_xV_2O_{5-y}$. Toward this end, we used a three-electrode coulometric titration arrangement:



(D)

From the very beginning, the emf of galvanic cell (D) (i.e., the emf between the reference and working electrodes) is equal to zero because the electrodes have the same composition ($x = 0.26$).

While passing the current between the lithium source and working electrode, lithium is electrochemically transferred through the solid electrolyte. Due to the high ionic and electronic conduction of bronzes, lithium ions distribute rapidly throughout the whole volume of the working electrode. The change in the working electrode composition can be calculated from Faraday's law if the mass of the sample and the amount of charge passed are known.

The emf of cell (D), appearing as the result of different compositions of working and reference electrodes due to coulometric titration, corresponds to the electrochemical reaction

$$\mathrm{Li}_{(Li_{0.26}V_2O_{5-y})} \rightarrow \mathrm{Li}_{(Li_xV_2O_{5-y})}, \tag{16}$$

where x express the working electrode composition after titration. Evidently,

$$\Delta G_{(16)} = -EF, \tag{17}$$

where E is emf of cell (D).

If $x < 0.26$ in Eq. (16), the potential of the working electrode is higher than that of the reference electrode ($E > 0$); consequently,

TABLE I

EXPERIMENTALLY FOUND VALUES OF FUNCTION $E(\text{mV}) = f(x, T)$ FOR CELL (D) ($P_{O_2} = 10^{-6.3}$ atm)

T	x				
(°K)	0.224	0.284	0.344	0.404	0.464
713	49.0	−32.0	−115.9	−199.4	−280.5
733	49.6	−32.5	−117.4	−202.0	−284.6
753	50.5	−32.9	−118.7	−204.5	−289.0
773	51.4	−33.2	−120.2	−207.1	−293.1
793	52.2	−33.8	−121.5	−209.6	−297.5
813	53.0	−34.1	−122.9	−212.2	−301.6
833	53.8	−34.6	−124.9	−214.9	−305.5

$\Delta G_{(16)} < 0$. On the contrary, if $x > 0.26$, $E < 0$ and $\Delta G_{(16)} > 0$.

The dependence of the emf of cell (D) on temperature was studied at several fixed x values (Table I). The changes of P_{O_2} in the range of 10^{-4} to $10^{-6.3}$ atm did not affect the emf within the experimental error (±0.2 mV).

It can be seen (Table I) that the relations $E = f(T)_{x=\text{const}}$ and $E = f(x)_{T=\text{const}}$ are both linear. It allowed one to present the experimental data as a linear equation with parameters x and T:

$$E = 165(\pm 3) - 654(\pm 5)x + 0.271(\pm 0.04)T - 1.015(\pm 0.015)xT \text{ (mV)}$$
$$(T = 713 \text{ to } 833°\text{K}, \quad P_{O_2} = 10^{-4} \text{ to } 10^{-6.3} \text{ atm}). \quad (18)$$

Therefore

$$\Delta G_{(16)} = -15\,900(\pm 300) + 63\,000(\pm 500)x - 26(\pm 4)T + 98(\pm 2)xT \text{ (J/mole).} \quad (19)$$

The dependence of $\Delta\bar{G}_{\text{Li}}$ on x and T values was found as the sum of Eqs. (12) and (19):

$$\text{Li}_{\text{met}} \rightarrow \text{Li}_{(\text{Li}_x\text{V}_2\text{O}_{5-y})}, \quad (20)$$

$$\Delta\bar{G}_{\text{Li}} = -365\,000(\pm 4000) + 63\,000(\pm 500)x - 36(\pm 5)T + 98(\pm 2)xT \quad \text{(J/mole).} \quad (21)$$

As distinct from $\Delta G_{(16)}$, $\Delta\bar{G}_{\text{Li}}$ is essentially negative in the entire range of β-phase homogeneity. On the contrary, the relative partial molar entropy of lithium $\Delta\bar{S}_{\text{Li}}$ evaluated from Eq. (21) as follows,

$$\Delta\bar{S}_{\text{Li}} = 36(\pm 5) - 98(\pm 2)x \quad \text{(J/mole} \cdot °\text{K),} \quad (22)$$

changes the sign: $\Delta\bar{S}_{\text{Li}} > 0$ at $x < 0.37$, and $\Delta\bar{S}_{\text{Li}} < 0$ at $x > 0.37$.

To determine the extent of the region of homogeneity of β-$\text{Li}_x\text{V}_2\text{O}_{5-y}$ depending on temperature, the temperature dependence of the emf of cell ($P_{O_2} = 10^{-6.3}$ atm)

$$\text{Pt}, \beta\text{-Li}_{0.26}\text{V}_2\text{O}_{5-y}|\text{Li}^+|(\beta+\gamma)\text{-Li}_{0.49}\text{V}_2\text{O}_{5-y}, \text{Pt} \quad \text{(F)}$$

was examined. A mixture of β- and γ-phases of $\text{Li}_{0.49}\text{V}_2\text{O}_{5-y}$ composition was prepared by coulometric titration in cell (D).

The results of this examination are presented in Table II. The tabulated data were used along with Eq. (18) to calculate the values of x, corresponding to the upper limit of the region of homogeneity of the β-phase. Within the experimental error, this value is independent of temperature and is $x = 0.467(\pm 0.002)$.

The independence of the upper limit of the homogeneity region of β-$\text{Li}_x\text{V}_2\text{O}_{5-y}$ on temperature agrees with the data available in the literature (*5*, *8*). As far as the value of $x_{\max}$ is concerned, some discrepancies occur: $x = 0.50$ (*5*), and $x = 0.55$ (*9*). We assume these discrepancies to result from the dependence of the $x_{\max}$ value on P_{O_2}; however, P_{O_2} was not controlled in the works discussed in Refs. (*5*, *8*).

Examination of the lower limit of the β-phase homogeneity region has also been done by emf measurements of the $(\alpha + \beta)$-

TABLE II

TEMPERATURE DEPENDENCE OF THE emf OF CELL (F) AND CALCULATED VALUES OF $x_{\max}$ (UPPER LIMIT OF THE HOMOGENEITY REGION OF β-$\text{Li}_x\text{V}_2\text{O}_{5-y}$)

T (°K)	E (mV)	$x_{\max}$
713	−283.8	0.466
733	−290.3	0.468
753	−293.2	0.467
773	−296.0	0.466
793	−302.9	0.468
813	−305.2	0.467
833	−309.0	0.467

$Li_xV_2O_{5-y}$ mixture with respect to $Li_{0.26}V_2O_{5-y}$ in the cell analogous to the (F) cell. The obtained value $x = 0.222(\pm 0.002)$ and its independence of temperature are consistent with the published data: $x = 0.22$ (*5, 8, 9*).

Conclusions

The relative partial molar free energy of lithium ($\Delta\bar{G}_{Li}$) in the β-$Li_xV_2O_{5-y}$ bronze has been studied in reversible cells with a lithium-conducting solid electrolyte using coulometric titration. The dependence of $\Delta\bar{G}_{Li}$ on temperature (713 to 833°K) and composition parameter x (0.26 to 0.46) was found to be linear. It has been established that $\Delta\bar{G}_{Li}$ in β-$Li_xV_2O_{5-y}$ depends weakly on the P_{O_2} value in the studied range of oxygen partial pressures (10^{-4} to $10^{-6.3}$ atm). The limits of the homogeneity range of β-$Li_xV_2O_{5-y}$ were substantiated by careful emf measurements independent of temperature (713 to 833°K) at fixed $P_{O_2} = 10^{-6.3}$ atm.

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