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**Chemical Thermodynamic Assessment
of the Li-U-O System for Possible
Space Nuclear Applications**

T. M. Besmann
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Chemical Technology Division

CHEMICAL THERMODYNAMIC ASSESSMENT OF THE Li-U-O SYSTEM
FOR POSSIBLE SPACE NUCLEAR APPLICATIONS

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CHEMICAL THERMODYNAMIC ASSESSMENT OF THE Li-U-O SYSTEM
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ABSTRACT

A thermochemical assessment of possible oxide fuel-lithium coolant interactions in conceptual 100-kW(e) space nuclear power reactors has been performed. Results of the evaluation indicate that in the event of a cladding breach the fuel and coolant will interact with extremely negative consequences. The lithium has the potential to reduce the fuel to metallic uranium. Differences in temperature within the coolant loop can drive oxygen and uranium transport processes.

INTRODUCTION

Nuclear power systems for space applications were the objective of extensive research and development activity from the early 1950s to 1972. This work was discontinued by the federal government in 1973 because space power requirements then identified could be met at lower cost by alternate technologies. In February 1983, a triagency agreement among the National Aeronautics and Space Administration (NASA), the Department of Defense (DOD), and the Department of Energy (DOE) created the SP-100 Program and rejuvenated the space reactor program. The SP-100 Program will be identifying design concepts for 100-kW(e) class reactors.

In 1984 the SP-100 Program identified three preliminary reactor concepts to provide 100 kW(e) of power in space with a system weighing less than 3000 kg, that would fit into one-third or less of the cargo bay of the shuttle, and that would have a seven-year, full-power, operational life. The concepts identified are liquid-metal-cooled fast reactors. Reactor coolant temperatures for these concepts range from 925 to 1550 K, with fuel cladding temperatures of 1100 to 1700 K. Power conversion

systems considered for these concepts are in-core thermionics, out-of-core thermoelectrics, and stirling cycle engines.

A major material consideration for these systems is the selection of the reactor fuel, cladding and structural alloy, and coolant. A fuel and coolant combination which continues to be considered for 100-kW(e) applications is $\langle \text{UO}_{2\pm x} \rangle^*$ and $\{\text{Li}\}$. An area of specific concern for this combination is the interaction of $\langle \text{UO}_{2\pm x} \rangle$ with $\{\text{Li}\}$ in the event of cladding failure. Although experimental data describing this reaction are limited, work carried out by Battelle in 1965 suggests negative consequences.¹ The objective of this report is to evaluate the available thermochemical data describing $\langle \text{UO}_{2\pm x} \rangle$ and the Li-O system and provide some observations regarding the interaction of $\langle \text{UO}_{2\pm x} \rangle$ and $\{\text{Li}\}$ at the proposed space reactor operating conditions.

THERMOCHEMICAL INFORMATION

An effective model for describing the relationship between oxygen partial pressure, temperature, and the stoichiometry of $\langle \text{UO}_{2\pm x} \rangle$ has been developed by Lindemer and Besmann² (Fig. 1). The model is also capable of predicting phase boundary locations and, as can be seen in Fig. 1, has predicted the oxygen partial pressure and temperature boundary between $\langle \text{UO}_{2-x} \rangle$ and $\langle \text{U} \rangle$ or $\{\text{U}\}$ containing dissolved oxygen.

Thermochemical data describing the solution of oxygen in $\{\text{Li}\}$ and the formation of $\langle \text{Li}_2\text{O} \rangle$ have been reviewed recently by Lindemer et al.³ The relationship between oxygen partial pressure, the concentration of oxygen dissolved in $\{\text{Li}\}$, and temperature has been assessed and is displayed in Fig. 2, along with the limit for formation of $\langle \text{Li}_2\text{O} \rangle$. For example, consider the line in Fig. 2 for $\{\text{Li}\}$ containing 10^4 wppm oxygen. At temperatures greater than 930 K, to the right of the intersection with the $\{\text{Li}\}$ - $\langle \text{Li}_2\text{O} \rangle$ line, only $\{\text{Li}\}$ is present. However, at temperatures less than 930 K, 10^4 wppm oxygen will cause the precipitation of $\langle \text{Li}_2\text{O} \rangle$

*The symbols $\langle \rangle$ and $\{ \}$ will denote solid and liquid phases, respectively.

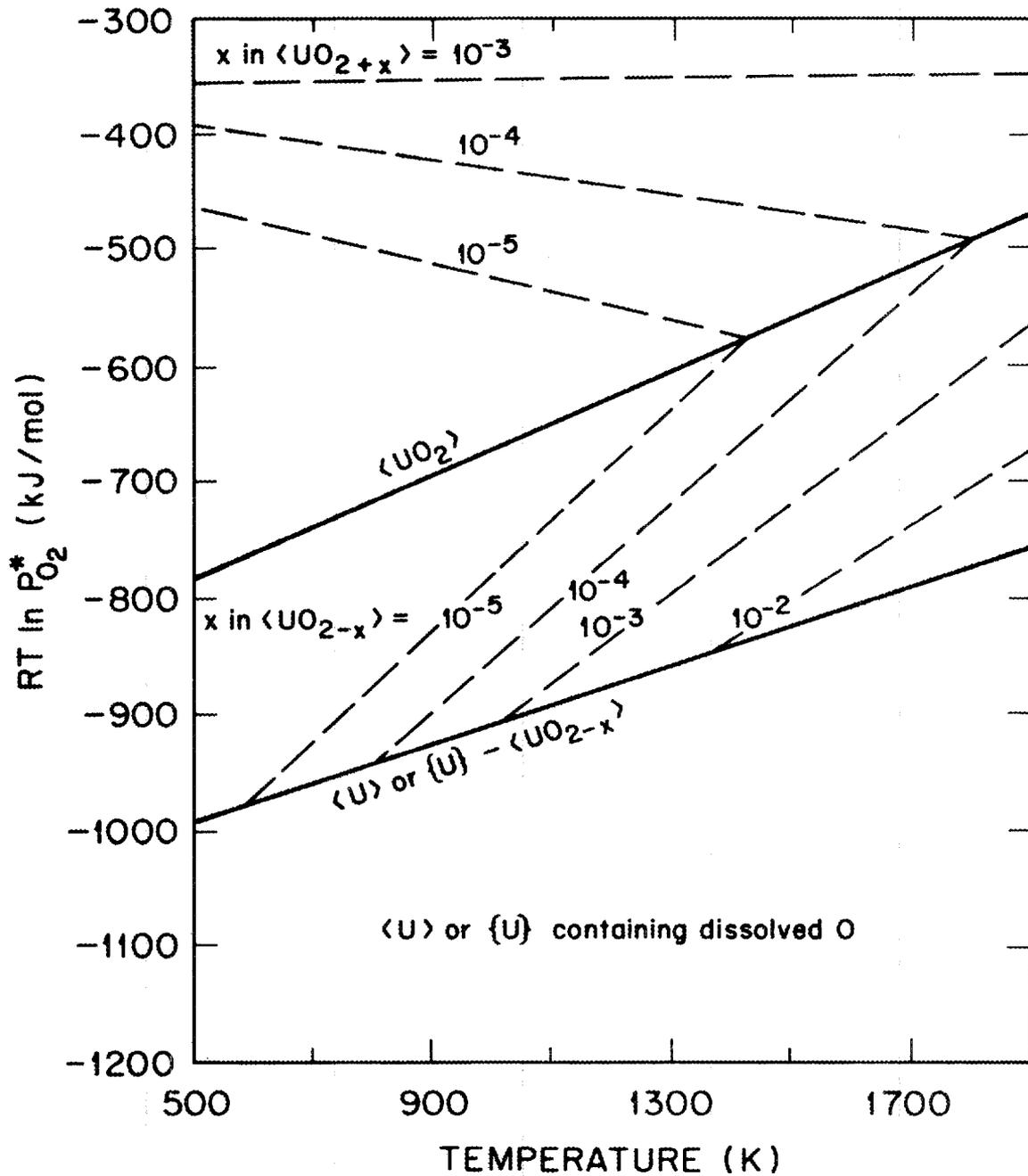


Fig. 1. Plot of temperature versus $RT \ln (P_{O_2}^*)$ (oxygen potential) in the U-O system after ref. 2, where R is the ideal gas law constant, T is absolute temperature, and $P_{O_2}^*$ is the ratio of the observed oxygen partial pressure to the reference state oxygen pressure (0.101 MPa or 1 atm).

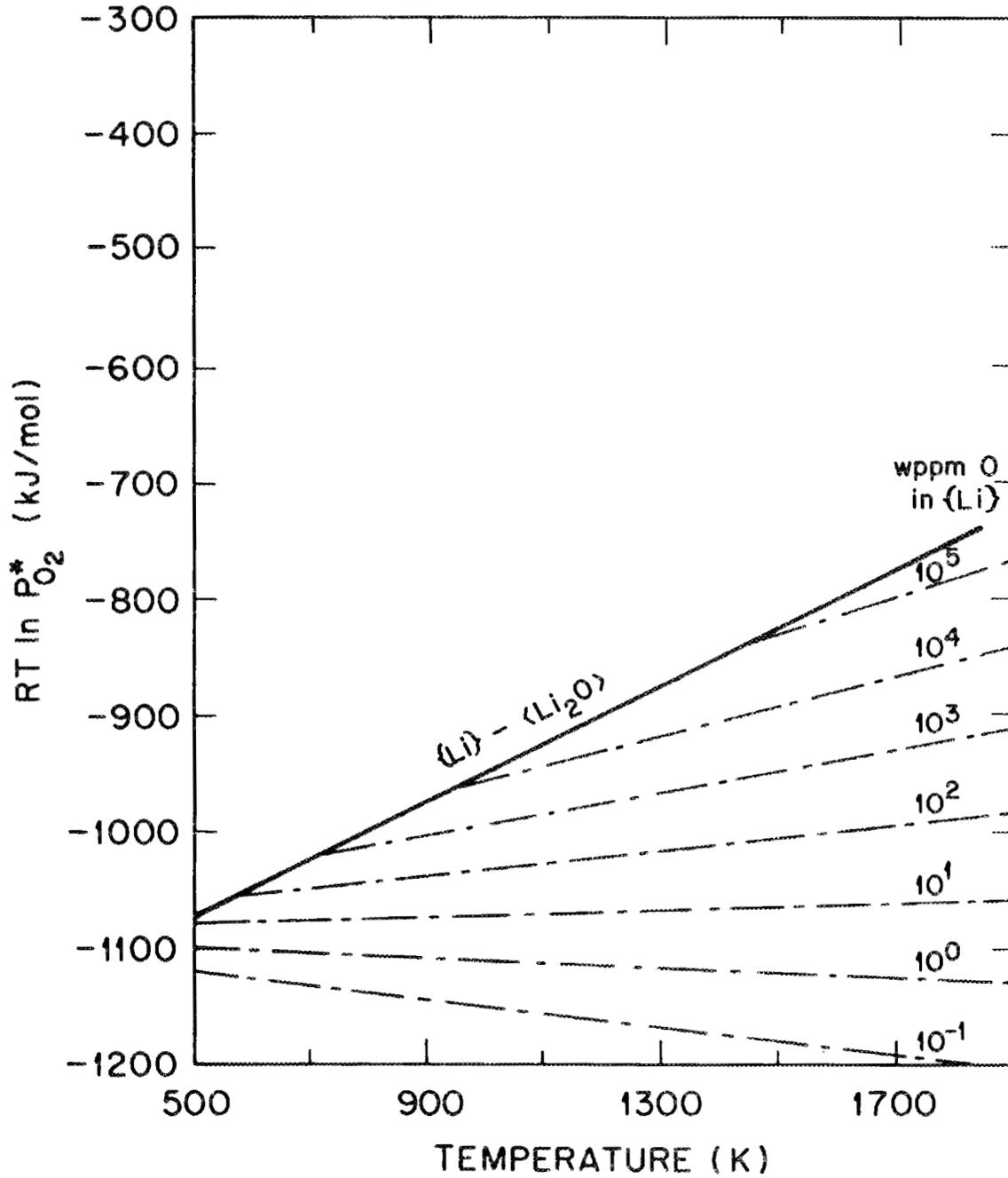


Fig. 2. Plot of temperature versus $RT \ln (P_{O_2}^*)$ (oxygen potential) in the Li-O system after ref. 3.

until the decreased solubility limit is reached. Of course, at oxygen partial pressures in excess of those indicated by the $\{Li\}$ - $\langle Li_2O \rangle$ line, the liquid metal is unstable and only $\langle Li_2O \rangle$ can exist.

The Li-U-O system is considered in depth in the assessment by Lindemer et al.³, from which the portion of the Li-U-O ternary phase diagram shown in Fig. 3 was obtained. The diagram is modified from that of Fig. 31 in Lindemer et al.³ as a result of an observed inconsistency with the thermodynamic values of the phases. Figure 3 displays the correct joins between $\langle UO_2 \rangle$ and $\langle Li_2O \rangle$ and between $\langle Li_2O \rangle$ and $\langle U \rangle$, as opposed to the original boundaries which connected $\langle Li_7UO_6 \rangle$ and $\{Li\}$ and $\langle UO_2 \rangle$ and $\{Li\}$.

The ternary phase which forms at the lowest oxygen partial pressure, and therefore in the region of interest for fuel systems, is $\langle Li_7UO_6 \rangle$. The minimum oxygen partial pressures and temperatures at which the phase is stable with $\langle UO_{2-x} \rangle$ and $\langle Li_2O \rangle$ are exhibited by the $\langle Li_7UO_6 \rangle$ - $\langle UO_{2-x} \rangle$ - $\langle Li_2O \rangle$ line in Fig. 4. Note that the melting point or decomposition temperature for $\langle Li_7UO_6 \rangle$ is unknown, and therefore the temperature at which the $\langle Li_7UO_6 \rangle$ - $\langle UO_{2-x} \rangle$ - $\langle Li_2O \rangle$ terminates is also unknown, although it is shown extending over the entire range.

The most effective means of assessing the Li-U-O interactions of interest for space reactors is to combine the $\langle UO_{2\pm x} \rangle$ information with that for Li-O. Such an overlay (Fig. 4) displays the phase behavior for the Li-U-O system at low oxygen partial pressures.

DISCUSSION

The thermochemical relationships between fuel and coolant are displayed in Fig. 4. From this information it appears that a failed $\langle UO_{2\pm x} \rangle$ fuel pin suffering the ingress of $\{Li\}$ can be expected to interact strongly. As noted by Adamson and Kangilaski⁴ and Kangilaski et al.¹ and confirmed by the relationships in Fig. 4, $\{Li\}$ will reduce $\langle UO_{2\pm x} \rangle$ to metallic uranium. There does exist a small region where $\langle UO_{2-x} \rangle$ can coexist with $\{Li\}$, in the area above ~ 1450 K where the

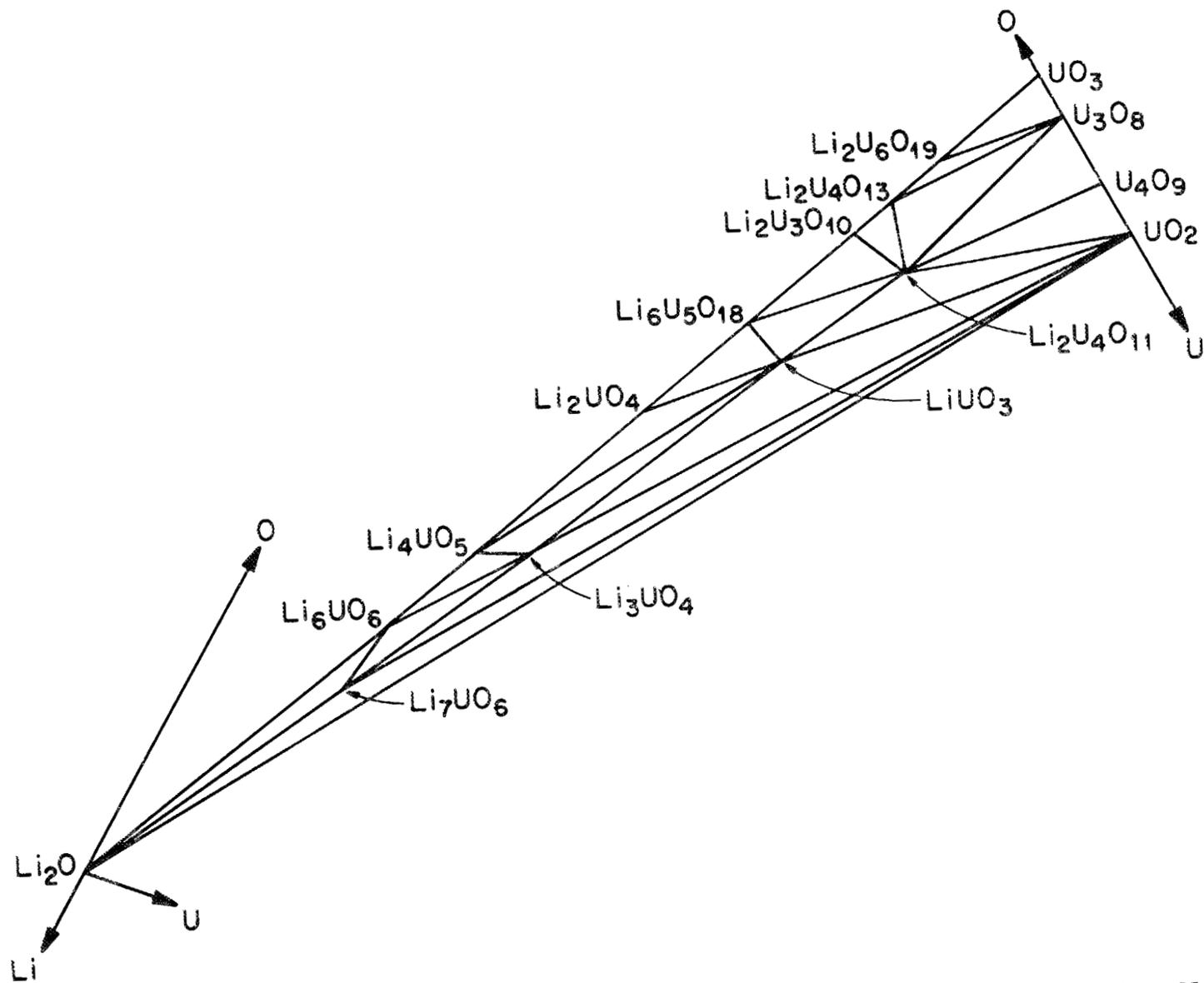


Fig. 3. The modified Li-U-O ternary equilibrium diagram for temperatures less than 950 K.

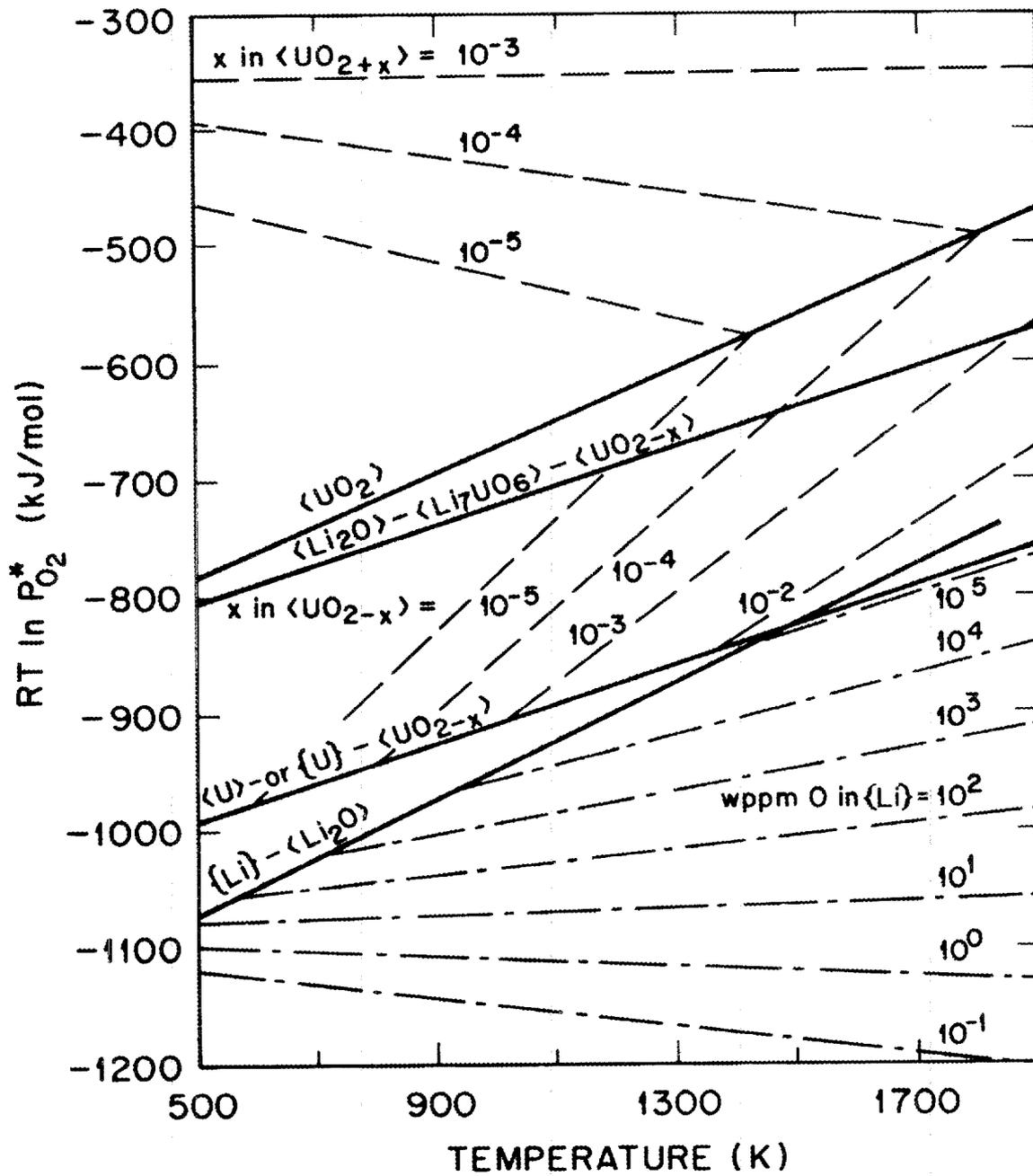


Fig. 4. Plot of temperature versus $RT \ln (P_{O_2}^*)$ (oxygen potential) for the Li-U-O system.

{Li}-<Li₂O> line lies above the {U}-<UO_{2-x}> line. This probably has little significance from a compatibility point of view because the {Li} present would have to contain an extremely high concentration of oxygen, approaching the content of the <Li₂O>, before the system could be maintained in this regime.

The only ternary phase that is stable in the system is <Li₇UO₆>, which may be viewed as a corrosion product of the interaction of <UO_{2±x}> and {Li}. The ternary phase is unstable in the presence of {Li}, and will likely only be observed in association with <Li₂O> and fuel having a stoichiometry near <UO₂>. Therefore, the formation of <Li₇UO₆> in {Li} predicted by Adamson and Kangilaski⁴ appears unlikely.

The information in Fig. 4 also has implications for the transport of uranium and oxygen in the coolant loop. Uranium can dissolve in {Li} at the higher temperature of the fuel pin and may alloy with the cladding and other structural metals, or perhaps even precipitate in cooler regions of the coolant loop should its solubility limit be reached.

The relationships described in Fig. 4 also raise the possibility of depositing <Li₂O> in lower temperature regions of the coolant loop, following a breach of the cladding. Relatively high concentrations of oxygen can dissolve in {Li} at high temperatures, as a result of <UO_{2±x}> being reduced. However, the solubility of oxygen in {Li} is substantially decreased in the lower temperature regions of the coolant loop, allowing the formation of <Li₂O>. For example at 1500 K, {Li} has the capacity to dissolve in excess of 10⁵ wppm oxygen. If {Li} having this concentration of oxygen is cooled to 1300 K in another region of the reactor, it can only maintain 5.8 × 10⁴ wppm oxygen in solution. The remaining oxygen is then forced to precipitate as <Li₂O>, depositing an unwanted solid in the reactor and providing a mechanism for continually removing oxygen from the fuel.

CONCLUSIONS

The thermochemical assessment of the Li-U-O system discussed here, as well as other experimental and calculational efforts,^{1,4} conclude that $\langle \text{UO}_{2+x} \rangle$ fuel and {Li} coolant will interact with extremely negative consequences should a fuel pin be breached. The {Li} will reduce the uranium dioxide to the metal, destroying the integrity of the fuel. The ternary-phase $\langle \text{Li}_7\text{UO}_6 \rangle$ decomposes in the presence of {Li} and therefore does not have the potential for forming a protective coating on the surface of the fuel. Substantial differences in temperature within the {Li} coolant loop may drive oxygen and uranium transport processes.

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