

# Heats of Solution/Substitution of Rb<sup>+</sup> and Cs<sup>+</sup> in TlI Crystal

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The heats of solution or substitution,  $\Delta H_s^\circ$ , of RbI and CsI in TlI crystal are reported, viz,  $-191.1$  and  $-209.7$  kJ mol<sup>-1</sup>, respectively, along with the recovered lattice energies,  $\Delta H_L^\circ$ , viz,  $-29.5$  and  $-49.5$  kJ mol<sup>-1</sup>, respectively, and compared with some mixed alkali iodides. The large negative  $\Delta H_s^\circ$  values are far removed from those of their mixed alkali iodides, while the  $\Delta H_L^\circ$  values show reasonable consistency.

## Introduction

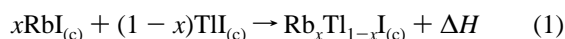
Physicochemical studies of the solid state usually involve impurities in crystals to some degree. A large class of phenomena and useful solid state devices depends on impurity or dopant presence.

Recently, we reported the structure stabilization or locking-in of the high-temperature *Pm3m* CsCl-type cubic structure of TlI to room temperature by incorporating 5 mol % Rb<sup>+</sup> and 7.5 mol % Cs<sup>+</sup>.<sup>2</sup> Yellow room temperature  $\beta$ -TlI, a double-layered orthorhombic structure related to NaCl,<sup>3</sup> transforms to red  $\alpha$ -TlI, with a *Pm3m* CsCl cubic structure, at 172 °C with transition enthalpy  $\Delta H_t = 865$  J mol<sup>-1</sup>. The  $\alpha$ -TlI structure above 172 °C is isomorphous with the room temperature-stable *Pm3m* structure of its analogs TlCl and TlBr. In other words, 5 mol % Rb<sup>+</sup> or 7.5 mol % Cs<sup>+</sup> provided the energy of 865 J/mol required to stabilize the *Pm3m* CsCl cubic structure of TlI at room temperature.

The incorporation of the isovalent Rb<sup>+</sup> or Cs<sup>+</sup> in TlI crystal lattice was thought to involve minimal change in the basic geometric structure of the crystal especially since CsI is isomorphous; i.e. space group *Pm3m*, with  $\alpha$ -TlI and  $r_{\text{Rb}^+} = 166$  pm, is quasi-equal to  $r_{\text{Tl}^+} = 164$  pm for coordination number = 6.<sup>4</sup> Solubility of a solute in a solvent is the practical quantity of interest, but the quantity of thermodynamic and more theoretical interest is the heat or energy of solution. It is interesting to consider the heats of solution in terms of TI<sup>+</sup> rearrangement or displacement which attends incorporation of Rb<sup>+</sup> or Cs<sup>+</sup> into the TlI lattice. To obtain the heat of solution, we proceed by determining the heat of reaction in which 1 mol of guest (Rb<sup>+</sup>, Cs<sup>+</sup>) dissolves in an infinite amount of host (TlI); this is the partial molar heat of solution of the guest in the host at infinite dilution. This heat quantity leads to the extra energy required to replace the lattice TI<sup>+</sup> by a Rb<sup>+</sup> or Cs<sup>+</sup>.

## Calculations for Solubility of RbI and CsI in TlI

One writes the chemical reaction of dissolving  $x$  mol of RbI in TlI as



When  $x$  is small,  $\Delta H/x$  is the partial molar heat of solution at infinite dilution rigorously expressed as

$$\left(\frac{\partial(\Delta H)}{\partial x}\right)_{x=0} = \lim_{x \rightarrow 0} \frac{\Delta H}{x} \equiv \chi \quad (2)$$

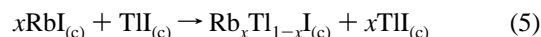
In terms of the heats of formation of the reactants and product, one can write

$$\begin{aligned} \chi &= \lim_{x \rightarrow 0} \frac{1}{x} [\Delta H_f^\circ(\text{Rb}_x\text{Tl}_{1-x}\text{I}) - \\ &\quad (1-x)\Delta H_f^\circ(\text{TlI}) - x\Delta H_f^\circ(\text{RbI})] \\ \chi &= \lim_{x \rightarrow 0} \frac{\Delta H_f^\circ(\text{Rb}_x\text{Tl}_{1-x}\text{I}) - \Delta H_f^\circ(\text{TlI})}{x} + \\ &\quad \Delta H_f^\circ(\text{TlI}) - \Delta H_f^\circ(\text{RbI}) \\ &= \Delta H_s^\circ + \Delta H_f^\circ(\text{TlI}) - \Delta H_f^\circ(\text{RbI}) \end{aligned} \quad (3)$$

where  $\Delta H_s^\circ$  is the change in heat content of the TlI lattice per mole of substituted RbI

$$\Delta H_s^\circ = \frac{[\Delta H_f^\circ(\text{Rb}_x\text{Tl}_{1-x}\text{I}) - \Delta H_f^\circ(\text{TlI})]}{x} = \chi - \Delta H_f^\circ(\text{TlI}) + \Delta H_f^\circ(\text{RbI}) \quad (4)$$

Also  $\Delta H_s^\circ$  is the heat of the reaction



It is understood that the  $\Delta H_f^\circ$  quantities are heats/enthalpies of formation from the elements in their standard thermodynamic states.

$\Delta H_s^\circ$  can also be called the heat/enthalpy of substitution since it is the change of TlI heat content resulting from the substitution of RbI, per mole of RbI. Besides the heat/enthalpy of substitution, one can view  $\Delta H_s^\circ$  as another interesting quantity, the “recovered lattice energy”,  $\Delta H_L^\circ$ . If one accepts the solution process as the destruction of 1 mol of RbI lattice and the creation of a new imperfect lattice, we want to know how much new lattice energy has been produced to compensate for the loss of the old, that is

$$\Delta H_L^\circ = \chi - \Delta H_{\text{fL}}^\circ(\text{TlI}) + \Delta H_{\text{fL}}^\circ(\text{RbI}) \quad (6)$$

where  $\Delta H_{\text{fL}}^\circ(\text{TlI})$  and  $\Delta H_{\text{fL}}^\circ(\text{RbI})$  are the heats of formation of the lattice from gas-phase ions, i.e.  $U_L = -\Delta H_{\text{fL}}^\circ$ .

Knowing that 5 mol % RbI stabilizes TlI in the CsCl cubic structure requiring 865 J mol<sup>-1</sup> we have

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$$\chi = \lim_{x \rightarrow 0} \frac{\Delta H}{x} = \frac{+865 \text{ J mol}^{-1}}{0.05} = +17\,300 \text{ J mol}^{-1} = +17.3 \text{ kJ mol}^{-1}$$

From the literature (ref 5) we have  $\Delta H_f^\circ(\text{TlI}) = -125.4 \text{ kJ mol}^{-1}$  and  $\Delta H_f^\circ(\text{RbI}) = -333.8 \text{ kJ mol}^{-1}$ , which when inserted into eq 4 yields  $\Delta H_s^\circ(\text{RbI}) = -191.1 \text{ kJ mol}^{-1}$ .

Similarly, for stabilization of TlI in the CsCl cubic structure by 7.5 mol % CsI, we have

$$\chi = \lim_{x \rightarrow 0} \frac{\Delta H}{x} = \frac{+865 \text{ J mol}^{-1}}{0.075} = +11\,533 \text{ J mol}^{-1} = +11.5 \text{ kJ mol}^{-1}$$

Using literature values  $\Delta H_f^\circ(\text{TlI}) = -125.4 \text{ kJ mol}^{-1}$  and  $\Delta H_f^\circ(\text{CsI}) = -346.6 \text{ kJ mol}^{-1}$  inserted into eq 4 we obtain  $\Delta H_s^\circ(\text{CsI}) = -209.7 \text{ kJ mol}^{-1}$ .

In terms of the recovered lattice energy,  $\Delta H_L^\circ$ , we have using  $\Delta H_L^\circ$  values for RbI and CsI from ref 6 and for TlI values calculated from the Born–Haber cycle

$$\Delta H_L^\circ(\text{RbI}) = +17.3 - 663.5 + 616.7 = -29.5 \text{ kJ mol}^{-1}$$

and

$$\Delta H_L^\circ(\text{CsI}) = +11.5 - 663.5 + 602.5 = -49.5 \text{ kJ mol}^{-1}$$

## Discussion

There has been a considerable amount of work, experimental and theoretical, on the substitution of an impurity/dopant of the same charge in ionic crystals. Most of these studies have been concentrated on mixed alkali halides mainly involving the NaCl structure. The main focus of these studies was to establish a procedure taking into account the dominant contributing factors, viz, force fields and potentials, etc., in the vicinity of the impurity leading to the theoretical calculation of the lattice energy of the impure crystal.

In some respects  $\text{Tl}^+$  resembles the alkali metals, especially  $\text{Rb}^+$  and  $\text{Cs}^+$ .<sup>3</sup> On this basis, any knowledge regarding the presence of RbI or CsI in TlI can be considered an extension of a mixed alkali halide system that can provide more insight into the thermodynamic and structural state of the impure crystal. Values of  $\chi$ ,  $\Delta H_s^\circ$ ,  $\Delta H_L^\circ$ , and  $-\Delta H_L^\circ$  for RbI–TlI, CsI–TlI, and NaI–KI binary systems are given in Table 1. The  $\chi$  and  $\Delta H_L^\circ$  values appear to be consistent within reasonable limits. However, the values of  $\Delta H_s^\circ$  for the TlI crystal are beyond limits of

**TABLE 1: Comparison of Heats of Solution ( $\text{kJ mol}^{-1}$ ) of RbI and CsI in TlI with Some Mixed Alkali Iodides<sup>a</sup>**

solvent (host)	solute (guest)	$\chi$ , solute	$\Delta H_L^\circ$	$\Delta H_s^\circ$	$\Delta H_L^\circ$ , solvent
TlI	RbI	17.3	−29.5	−191.1	663.5
TlI	CsI	11.5	−49.5	−209.7	663.5
NaI	KI	13.4	−42.2	67.9	682.8
KI	NaI	9.6	65.2	−37.7	627.2

<sup>a</sup> Reference 7.

comparison with NaI and KI. It has been suggested that when a larger ion replaces a smaller one the value of  $\Delta H_s^\circ$  is positive, but this is not the case with  $\text{Rb}^+$  and  $\text{Cs}^+$  in TlI with large negative  $\Delta H_s^\circ$  values. This general positive value  $\Delta H_s^\circ$  correlation with larger solute ion substitutions does not take into account the host structure where the NaCl structure is in strong contrast to the CsCl structure. Consistent with our negative  $\Delta H_s^\circ$  values are those for alkali earth halides in alkali halides<sup>8</sup> where a higher concentration of vacancies is expected. On this same point it has been noted that mixed crystals of alkali halides can contain a substantially higher concentration of vacancies than the pure component crystals.<sup>9</sup> However, the  $\Delta H_L^\circ$  values are consistently negative for a larger solute ion indicating a smaller lattice energy for the impure crystal than for the pure host crystal.

In summary, we have presented heats of solution/substitution and recovered lattice energies for  $\text{Rb}^+$  and  $\text{Cs}^+$  in TlI. Hopefully, these data will provide another positive step along with existing mixed alkali halide data toward the theoretical analysis and understanding of the crystalline solution.

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## References and Notes

- (1) Huang, P.-N.; Secco, E. A. *J. Solid State Chem.* **1993**, *103*, 314.
- (2) Secco, E. A.; Sharma, Anita *J. Phys. Chem. Solids* **1995**, *56*, 251.
- (3) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; p 272.
- (4) Shannon, R. D. *Acta. Crystallogr.* **1976**, *A32*, 751.
- (5) National Bureau Standards Technical Notes 270-3–270-8. *CRC Handbook of Chemistry and physics*; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1988.
- (6) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; p 96.
- (7) Douglas, T. B. *J. Chem. Phys.* **1966**, *45*, 4571.
- (8) Barr, L. W.; Lidiard, A. B. Defects in ionic crystals. In *Physical Chemistry—An Advanced Treatise*; Eyring, H., Henderson, D., Jost, W., Eds.; Academic Press: New York, 1970; Vol. 10.
- (9) Johannesen, Ø; McKelvy, M. *J. Phys. Chem. Solids* **1986**, *47*, 265 and references therein.