

## **Response to the Comments by P. Bopp and M. Wolfsberg**

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We agree with the Bopp and Wolfsberg analysis<sup>(1)</sup> of the box 'model for isotope effects on Henry's law constants in aqueous solution.' In fact, one of us (RHR), independently had derived the same result as Bopp and Wolfsberg in a slightly different way. The Bopp and Wolfsberg/Romer analysis shows that the theoretical expression suggested by one of us, and used by Muccitelli and Wen,<sup>(2)</sup> Benson, Krause, and Peterson,<sup>(3)</sup> and Benson and Krause<sup>(4)</sup> to infer the dimensions of the hypothetical cubical box in water from measurements of isotopic fractionation, was incorrect and that their calculations of box sizes were consequently in error. Analysis of our experimental results using the correct theory for the box model shows that not only does the calculated size of the box depend on the solute molecule, which ought not to be the case if the box model were applicable, but, in addition, the calculated box dimensions, especially for oxygen, are implausibly large for possible cavities in water.

We wish to add a few comments to those of Bopp and Wolfsberg. The 'box model' referred to here is one in which the potential for a solute molecule is constant within a cubical region, rising abruptly to infinity at the boundaries of the 'box.' When the correct theory for the box model in this simplest form gave implausible cavity dimensions, the question arose as to whether this might be due to some of the mathematically convenient but physically unreasonable features of this potential. There is, for instance, no physical justification for choosing a cubical shape for the interior of the box; we therefore repeated the calculations for a box of spherical shape with similar lack of success in

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interpreting the experimental results. In addition, we thought it possible that anomalies could be produced by the physically unreasonable infinite discontinuity in potential at the edges of the box. Pursuing this possibility, we calculated partition functions for a one-dimensional problem in which a particle is subject to a potential  $V(x) = V_0 \cot^2(\pi x/a)$ ,  $0 < x < a$ , where  $V_0$  is small but not zero.<sup>(5)</sup> This potential rises rapidly but not discontinuously to infinity at  $x=0$  and  $x=a$  and is thus a 'smoothed' approximation to the usual infinite square well potential; partition functions calculated for this problem, however were little different from those calculated for the conventional one-dimensional box. This result, though obtained only for a one-dimensional problem, suggests that the impossibility of understanding our experimental results in terms of the box model does not arise from the abrupt infinite discontinuity of the potential used in that model.

We, too, have explored the application of the harmonic potential model to the isotopic fractionation of gases during solution. The results will be submitted for publication later.

## REFERENCES

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