TABLE I. A comparison of enthalpies of evaporation and anion diffusion in some alkali halide single crystals.

Substance	Activation enthalpy of evaporation (eV)	Activation enthalpy of anion diffusion (eV)
KBr (pure)	2.2[a,b]	2.2[f]
KCl (pure)	2.2[c]	2.12[g]
NaCl (pure)	2.3[d,e]	2.12,[h] 2.2,[i] 2.3[j]
NaCl (300 ppm Ca)	2.7[d,e]	2.5,[h] 2.5–2.6[i]

[a] See Ref. 1.
[b] Evaporation in low pressure gas.
[c] R. S. Bradley and P. Volans, Proc. Roy. Soc. (London) A217, 508 (1953).
[d] See Ref. 2.
[e] Average values calculated from the data in Ref. (2).
[f] L. W. Barr and D. K. Dawson (unpublished).
[g] R. G. Fuller, Phys. Rev. 142, 524 (1966).
[h] See Ref. 4.
[i] See Ref. 3.
[j] L. G. Harrison, J. A. Morrison, and R. Rudham, Trans. Faraday Soc. 54, 106 (1958).

If evaporation is envisaged as being controlled by the rate at which anions jump on to the surface to become adions, leaving behind a vacancy, then a rough estimate can be made of the constant of proportionality.

The assumption is made that evaporation does not alter the equilibrium vacancy concentration. In equilibrium, with no evaporation, the number of vacancies arriving at the surface is equal to the number departing, and because of the continuity of vacancy flux, each is equal to the number crossing unit area of a (100) plane in the bulk of the crystal in one direction. An *upper* limit to the evaporation rate is then obtained by setting the number of molecules evaporating equal to the equilibrium value of the number of anion vacancies *leaving* the surface in 1 sec.

The random-walk expression for the diffusion coefficient in terms of the atomic jump frequency Γ and the jump distance r is, neglecting correlation effects,[7]

$$D = \tfrac{1}{6}\Gamma r^2.$$

The evaporation rate is then given by

$$E \lesssim \alpha \Gamma N m = 6\alpha N m D/r^2.$$

Here N is the number of anions per square centimeter, m is the molecular mass, and α is a numerical factor which arises, since jumps in only one direction are counted. For single vacancies in an fcc lattice $\alpha = \tfrac{1}{3}$, for a cubic lattice $\alpha = \tfrac{1}{6}$.

In view of the crude nature of the calculation we write

$$E \lesssim (Nm/r^2)D.$$

Evaluating this for NaCl gives $Nm/r^2 \sim 4 \times 10^7$ g cm^{-4}, to be compared with the empirical value of 6×10^5 g cm^{-4}.

Possible tests of this hypothesis can be suggested. The evaporation rate in NaCl should vary with divalent cation content in the same way as anion diffusion[4] and should be virtually independent of impurity content above ~ 100 ppm. KCl should behave like NaCl. Measured anion diffusion rates in KBr suggest that in divalent doped KBr the evaporation rate should be depressed by a factor of 2 and the activation enthalpy virtually unchanged. However, the best test would probably be the evaporation of cesium halides. Since in these salts cation diffusion (activation enthalpy 1.5 eV) is the slower,[8] doping with divalent cations should initially *enhance* the evaporation rate. If the necessary diffusion data were available, a study of evaporation of CsCl above and below the crystallographic transition might be informative.

If the conjecture is confirmed, measurement of evaporation rates in pure and doped ionic solids might yield information on the relative amounts of single and vacancy pair diffusion in cases where suitable tracers are unavailable.

I should like to thank A. D. Le Claire for many helpful comments.

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[6] D. K. Dawson and L. W. Barr, Proc. Brit. Ceram. Soc. 9, 171 (1967).
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Determination of the Well Depth for Weak Intermolecular Potentials*

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Milne and Greene[1] proposed to measure mass spectrometrically the enthalpy of dimerization of rare-gas atoms and from such measurements to determine the well depth for the interaction more precisely than from the analysis of gaseous p–V–T and transport data. In this comment we wish to show the connection between the proposed method and standard gas theory, to point out that the method of reducing the enthalpy of dimerization to a well depth has been used before, and finally to show that recent analyses of virial and

transport data have produced well depths in much closer agreement than the authors claim.

Every gas can be considered ideal if it is taken to be a mixture of clusters of molecules.[2] If we let N_j be the number of clusters with j molecules, then for an ideal multicomponent mixture

$$pV = kT \sum N_j, \qquad (1)$$

with $\sum j N_j = N$. If we then introduce an equilibrium constant K_j for each j cluster in terms of its partial pressure, express each partial pressure in terms of N_j/V by the Gibbs–Dalton rule, and substitute back into Eq. (1), we obtain an equation of state of the virial form with the virial coefficients given in terms of the K_j,

$$B = -K_2 RT, \qquad C = -2(K_3 - 2K_2^2)(RT)^2, \text{ etc.} \quad (2)$$

A rigorous statistical-mechanical treatment shows these relations to be formally exact, with the K_j proportional to the corresponding Mayer cluster integrals.[3,4]

The enthalpy of formation of the dimer is related to the temperature dependence of K_2 by the Gibbs–Helmholtz equation

$$\frac{\Delta H_2}{R} = \frac{d \ln K_2}{d(1/T)}. \qquad (3)$$

From Eqs. (2) and (3) we find

$$\frac{\Delta H_2}{R} = \frac{T}{B} \frac{d(B/T)}{d(1/T)} = \frac{\mu C^\circ_p T}{-B}, \qquad (4)$$

where μ is the Joule–Thomson coefficient. Thus measurement of ΔH_2 is equivalent to measurement of the

TABLE I. Potential well depths for Ar from gas data.

Potential type	Well depth (cal/mole)	Reference
Multiparameter	286	a
Exp–6	302	b
Kihara	293	b
Kihara	284	c
Kihara	274	d
Multiparameter	278	e
Multiparameter	292	f
Multiparameter	296	g
Morse	264	h
Multiparameter	294	i

[a] R. J. Munn, J. Chem. Phys. 40, 1439 (1964).
[b] A. E. Sherwood and J. M. Prausnitz, J. Chem. Phys. 41, 429 (1964).
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[i] J. A. Barker and A. Pompe, Australian J. Chem. 21, 1683 (1968).

second virial coefficient as a function of temperature and contains neither more nor less information on the potential well.

Epstein,[5] in a theoretical study of the low-temperature second virial coefficients for a Lennard-Jones gas, appears to be the first person to relate the enthalpy of dimerization to a well depth. He attributed the idea to W. H. Stockmayer. Epstein's series expansions might furnish a simpler method of extrapolating ΔH_2 to $T = 0$ than the numerical solution of the Schrödinger equation suggested by Milne and Greene. Thirteen years later Davies, Mason, and Munn[6] used the method to obtain the well depth of the potassium dimer in its singlet state. They actually knew a spectroscopic value of the dissociation energy and the temperature dependence of the second virial coefficient of potassium vapor, and they used the relationship of Eq. (4) as a consistency check (neglecting the zero-point energy). The extrapolation to $T = 0$ was performed by curve-fitting the virial data.

Finally, we note that Milne and Greene claim that their proposed method will yield the well depth within ± 40 cal/mole, and that this should be compared with values for argon, say, ranging from 100–300 cal/mole as determined from gaseous p–V–T and viscosity data. In recent years, however, such analyses have become quite refined, and the maximum spread of the values determined within the past five years is only about 40 cal/mole, as shown in Table I, which is better accuracy than is claimed for the new method.

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[4] T. L. Hill, Introduction to Statistical Thermodynamics (Addison-Wesley Publishing Co., Reading, Mass., 1960), Chap. 15.
[5] L. F. Epstein, J. Chem. Phys. 20, 1670 (1952).
[6] R. H. Davies, E. A. Mason, and R. J. Munn, Phys. Fluids 8, 444 (1965).

Reply to Comment on Determination of the Well Depth for Weak Intermolecular Potentials

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Spurling and Mason[1] have made two major comments regarding our mass-spectrometric method of determining well depths for weak intermolecular potentials. First, they state that the method proposed is equivalent to measurement of the temperature dependence of the second virial coefficient and contains neither more nor less information on the potential well. They argue that $B = K_2 RT$, where K_2 is an equilibrium constant for the