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Expression for predicting liquid evaporation flux: Statistical rate theory approach

C. A. Ward* and G. Fang†
Thermodynamics and Kinetics Laboratory, Department of Mechanical and Industrial Engineering, University of Toronto,
5 King's College Road, Toronto, Ontario, Canada M5S 3G8

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Recent measurements of the conditions existing at the interface of an evaporating liquid have found that the temperature approximately one mean free path from the interface in the vapor was *higher* than the temperature of the liquid at the interface. The measured temperature discontinuity at the interface is in the *opposite* direction of that predicted by several recent studies based on classical kinetic theory. A theoretical approach based on the transition probability concept of quantum mechanics, called statistical rate theory (SRT), is used herein to develop an expression for predicting the evaporation flux. The expression obtained is free of any fitting parameters. When applied to predict the conditions at which a particular value of the evaporation flux is expected and the result compared with the measurements at 15 different experimental conditions, it is found that the SRT expression accurately predicts the conditions. [S1063-651X(98)11412-5]

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I. INTRODUCTION

Recently, models of the Boltzmann equation have been used to predict the conditions existing at the interface of an evaporating liquid. It was predicted that the liquid could evaporate only if the temperature in the vapor were *less* than that in the liquid at the interface [1,2]. However, recent experimental studies have found the opposite relation between the temperature in the vapor at the interface and that in the liquid during steady-state evaporation. Using two different experimental arrangements, a series of 20 experiments have been conducted with water evaporating at different rates [3,4]. In each experiment, the temperature in the vapor at the interface was found to be *greater* than that in the liquid. In one experiment, the temperature in the vapor was measured within one mean free path of the water surface and under steady-state conditions it was found to be *higher* than that in the liquid by as much as 7.8 K.

It is reasonable to suppose that the disagreement between the results obtained from classical kinetic theory and the measurements results from the boundary conditions that were assumed in order to generate solutions to the Boltzmann equation. However, there is no method available in classical kinetic theory that can be used to derive the boundary conditions. Rather they are assumed and none of the boundary conditions considered have supposed that the temperature of the molecules leaving the liquid were other than the temperature of the liquid.

Since there is no apparent explanation for the observations based on classical kinetic theory, we investigate the possibility of predicting the conditions existing at the interface of an evaporating liquid using statistical rate theory (SRT) [5–13]. This theoretical approach is based on the transition probability concept as defined in quantum mechanics and uses the Boltzmann definition of entropy to introduce a thermodynamic description of the system. It has been applied in the past to predict the rate of gas absorption by a liquid [5,9], the rate of electron transport between ions in solution [7], and the rate of gas adsorption on single crystal metal surfaces [8,10]. In each case, it was found that after the molecular and material (or equilibrium) properties of the systems considered had been established, SRT could be used to predict the rate of the kinetic process. However, in each case the transport process took place under conditions that could be approximated as isothermal.

A more rigorous test of the statistical rate theory approach was reported recently when thermal desorption of CO from Ni(111) was examined [10,11]. Using the equilibrium isotherms for this system, the value of the material properties required to specify the chemical potential of CO adsorbed on this single crystal surface were determined [12]. The values of the material properties were incorporated in the SRT equations to obtain the expression for the rate of CO transport to the Ni(111) surface. These equations were then applied to examine temperature programmed desorption (TPD) experiments.

The TPD experiments were completely independent of the experimental circumstance from which the molecular and material properties had been established. It was found that over a range of initial surface concentrations of CO on Ni(111), the SRT equations could be used to accurately predict the measured TPD spectra of the system [11]. In this case then, the temperature at the interface was changed as a function of time, but the temperature of the surface and of the gas was the same at any instant during the process.

In the evaporation process, the temperature at the interface has been found experimentally to have a different value in the liquid than in the vapor. In order for SRT to be applied under this circumstance it must be extended to take account of the temperature in the phases at the interface being different. After this extension is made, it is found that the expression for the evaporation rate has a different dependence on the thermodynamic properties at the interface in each of the phases from that obtained from solutions of the Boltzmann

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*Author to whom correspondence should be addressed. FAX: 416-978-7322. Electronic address: ward@mie.utoronto.ca

†Present address: Trojan Technologies, Inc., 3020 Gore Road, London, Ontario, Canada N5V 4T7.

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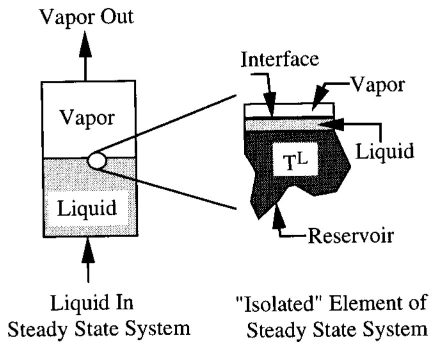

FIG. 1. Schematics of the steady-state system and the related isolated system. The isolated system is defined from the properties existing in the steady-state system at the liquid-vapor interface.

equation. For example, the SRT equations indicate that the liquid can evaporate even if the temperature in the vapor is greater than that in the liquid at the interface. This difference can be traced to the application of the quantum mechanical transition probability concept in the SRT approach. The SRT approach leads to an expression for the rate of evaporation that is free of any fitting constants and the predictions following from the expression can be directly compared with the observations of Refs. [3] and [4].

II. STATISTICAL RATE THEORY EXPRESSION FOR THE RATE OF EVAPORATION

Consider the single-component system shown schematically in Fig. 1 in which evaporation is occurring under steady-state conditions. We suppose the temperature and pressure in the vapor at the interface are T^V, P^V and those in the liquid are T^L, P^L. The energy required to maintain the temperature in the liquid at the interphase constant at T^L is supplied by its surroundings [3,4]. We propose to develop an expression for the evaporation flux that is in terms of these properties and the molecular and material properties of the substance that is evaporating.

A. An isolated system at an instant in time

Consider a small volume that consists of vapor and liquid phases in contact with a thermal reservoir that has a temperature T^L (see Fig. 1). Within the small volume, we suppose the interphase may be approximated as a surface and take the position of the surface to be such that there is no adsorption. Thus a molecule is in either the liquid phase or the vapor phase. We assume that the phases are each uniform up to the surface and that the intensive thermodynamic properties of each phase are constant over the extent of the respective phases. We take the depth of a phase to be δL^α, where α is either L or V, and the cross-sectional area of the surface to be δA. The limits on δL^α are discussed below.

At an instant t, let the number of molecules in the liquid and in the vapor be denoted as N^L and N^V and the temperature in the liquid and vapor phases of the small volume at this instant be the same as those in the steady-state system, T^L, T^V. We assume that the local equilibrium variables may be used to describe the thermodynamic state of each of the respective phases; thus the pressures in each phase of the small volume may be taken to be the same as those in the steady-state system. Our central assumption is that at this instant, the evaporation rate in the small system is the same as that in the steady-state system. Thus, if an expression for the rate of evaporation is developed for the small volume that is valid at the instant t, the expression may be applied in the steady-state system at any time.

Note that the small volume and reservoir form an isolated system and that their properties are defined from conditions existing in the steady-state system. The statistical rate theory approach may now be applied to obtain the expression for the rate of evaporation in the small volume at the instant t. An important element of this approach is the final, thermodynamic equilibrium state of the isolated system [5–7]. Based on the properties of the small system, the final temperature in this state will be T^L and the final pressure in the vapor phase P_e^V. This pressure is different from the instantaneous pressure P^V (see below).

B. Rate of interfacial molecular transfer

Since the local equilibrium approximation has been adopted, each phase of the small volume may be treated as a canonical ensemble system. Each portion of the small volume has a known temperature; thus each has a limited range of quantum mechanical energies ΔE^α. This range is defined by

$$(\Delta E^\alpha)^2 = \overline{(E^\alpha)^2} - (\overline{E}^\alpha)^2, \tag{1}$$

where the ensemble average of the energy $\overline{E}^\alpha$ is equal to the internal energy of phase α, U^α, and the ensemble average of the square of the energy is denoted as $\overline{(E^\alpha)^2}$. The energy range for each phase may be expressed

$$(\Delta E^\alpha) = \pm T^\alpha \sqrt{k C_V^\alpha}, \quad \alpha = L \text{ or } V, \tag{2}$$

where C_V^α is the constant volume specific heat of phase α. The possible quantum mechanical states of the phase α would be those with energies of $U^\alpha \pm \Delta E^\alpha$.

In the small volume at the instant t, the molecular distribution λ_j is such that there are N^L molecules in the liquid phase and N^V in the vapor phase. Let the number of quantum mechanical states of the isolated system (small volume and thermal reservoir) corresponding to λ_j that are within the energy range of the small volume be denoted as $\Omega(\lambda_j)$. If $u_v(\lambda_j)$ denotes one of these states, then

$$1 \leqslant v \leqslant \Omega(\lambda_j). \tag{3}$$

These states are viewed as unperturbed states. At the instant t, there is a virtual molecular distribution λ_k corresponding to the transfer of a molecule from the liquid phase to the vapor:

$$\lambda_k: \quad N^L - 1, N^V + 1. \tag{4}$$

Let the number of quantum mechanical states of the isolated system corresponding to this distribution be denoted as $\Omega(\lambda_k)$, and an unperturbed quantum mechanical state of this distribution as $u_\epsilon(\lambda_k)$. Then

$$1 \leqslant \epsilon \leqslant \Omega(\lambda_k). \tag{5}$$

For the small volume, the probability per unit area for a transition from a state corresponding to molecular distribution λ_j to a state corresponding to molecular distribution λ_k may be obtained from a first-order perturbation analysis of the Schrödinger equation [6,7]. If the isolated system is known to be in one of the quantum mechanical states of molecular distribution λ_j at the instant t and then the perturbation is imposed for a time δt, one finds that the result $K[\lambda_j(u_v),\lambda_k(u_\epsilon)]$ may be written

$$K[\lambda_j(u_v),\lambda_k(u_\epsilon)] = \frac{(2\pi)|V_{v\epsilon}|^2 \zeta\, \delta t}{\hbar\, \delta A}, \tag{6}$$

where ζ is the energy density of the states, $|V_{\nu\epsilon}|$ is the matrix element corresponding to a transition from a state of λ_j to a state of λ_k, $\hbar$ is the Planck constant divided by 2π, and we have assumed

$$\delta t(\Delta E^L + \Delta E^V) \geqslant 2\pi\hbar. \tag{7}$$

We take $K[\lambda_j(u_v),\lambda_k(u_\epsilon)]$ to be constant for all of the quantum mechanical states of the possible molecular distributions that are within the energy range of the small volume, $\Delta E^L, \Delta E^V$, and denote it as k_{LV} [6,7]. The probability of a transition from λ_j to molecular distribution λ_k at any instant in the interval δt, denoted as $\tau[\lambda_j,\lambda_k]$, would be the product of the probability of finding the system in a quantum mechanical state of molecular distribution λ_j at the instant t with the probability of a transition at any instant to any quantum mechanical state of the distribution λ_k times the number of states corresponding to distribution λ_k:

$$\tau[\lambda_j,\lambda_k] = \frac{k_{LV}\Omega(\lambda_k)\,\delta A}{\Omega(\lambda_j)\,\delta t}. \tag{8}$$

If the Boltzmann definition of entropy is assumed valid and introduced into Eq. (8), one obtains

$$\tau[\lambda_j,\lambda_k] = \frac{k_{LV}\delta A}{\delta t} \exp\left[\frac{S(\lambda_k) - S(\lambda_j)}{k}\right], \tag{9}$$

where $S(\lambda)$ is the entropy of the isolated system when the small volume is in molecular distribution λ and k is the Boltzmann constant.

At the same time that there is a probability of a transition from λ_j to λ_k, there is a probability for a transition corresponding to the transfer of a molecule from the vapor to the liquid phase. Suppose that this virtual molecular distribution is denoted as λ_i, where

$$\lambda_i: \quad N^L + 1, N^V - 1. \tag{10}$$

Following the procedure outlined above, one finds

$$\tau[\lambda_j,\lambda_i] = \frac{k_{VL}\delta A}{\delta t} \exp\left[\frac{S(\lambda_i) - S(\lambda_j)}{k}\right]. \tag{11}$$

When the molecular distribution changes from λ_j to distribution λ_k, the number of molecules in the liquid phase is changed,

$$N^L(\lambda_k) - N^L(\lambda_j) = -1, \tag{12}$$

and the number of molecules in the vapor is changed,

$$N^V(\lambda_k) - N^V(\lambda_j) = 1. \tag{13}$$

The entropy change of the isolated system when the molecular distribution changes from λ_j to λ_k may be expressed

$$S(\lambda_k) - S(\lambda_j) = \sum_{i=L,V,R} [S^i(\lambda_k) - S^i(\lambda_j)], \tag{14}$$

where the superscript R indicates the reservoir. Since we have assumed that the local equilibrium variables act as the independent variables for the entropy of each phase and the reservoir, the Euler relation may be applied to obtain

$$S^i = \frac{H^i}{T^i} - \frac{\mu^i N^i}{T^i}, \tag{15}$$

where H and μ denote the enthalpy and the chemical potential. We assume that neither the chemical potential nor the temperature of the respective phases is changed as a result of the change from molecular distribution λ_j to λ_k. Since there is no exchange of molecules between the small volume and the reservoir, by applying Eq. (15) in Eq. (14), one finds

$$S(\lambda_k) - S(\lambda_j) = \left(\frac{H^L(\lambda_k)}{T^L} - \frac{H^L(\lambda_j)}{T^L}\right) + \left(\frac{H^V(\lambda_k)}{T^V} - \frac{H^V(\lambda_j)}{T^V}\right) + \left(\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V}\right) + \left(\frac{U^R(\lambda_k)}{T^L} - \frac{U^R(\lambda_j)}{T^L}\right), \tag{16}$$

where we have taken advantage of the fact that the reservoir does not change pressure or volume. When the molecular distribution changes from λ_j to λ_k, one molecule in the small volume changes phase. The condition for the reservoir and system to form an isolated system is that

$$[H^L(\lambda_k) - H^L(\lambda_j)] + [H^V(\lambda_k) - H^V(\lambda_j)] + [U^R(\lambda_k) - U^R(\lambda_j)] = 0. \tag{17}$$

After substituting Eq. (17) into Eq. (16), one finds

$$S(\lambda_k) - S(\lambda_j) = \left(\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V}\right) + \left(\frac{1}{T^V} - \frac{1}{T^L}\right)[H^V(\lambda_k) - H^V(\lambda_j)]. \tag{18}$$

The total enthalpy of each phase H may be expressed in terms of the enthalpy per molecule h by introducing the number of molecules in each phase

$$H^i = h^i N^i, \quad i = L, V; \tag{19}$$

then Eq. (18) may be written

$$S(\lambda_k) - S(\lambda_j) = \left(\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V}\right) + h^V\left(\frac{1}{T^V} - \frac{1}{T^L}\right). \tag{20}$$

Following the same procedure, the entropy change for a molecular transition from distribution λ_j to λ_i is found to be

$$S(\lambda_i)-S(\lambda_j)=-[S(\lambda_k)-S(\lambda_j)]. \tag{21}$$

Thus

$$S(\lambda_i)-S(\lambda_j)=-\left(\frac{\mu^L}{T^L}-\frac{\mu^V}{T^V}\right)-h^V\left(\frac{1}{T^V}-\frac{1}{T^L}\right). \tag{22}$$

Note that the expression for the change in entropy between distributions λ_j and λ_k and between λ_j and λ_i are given in terms of the intensive thermodynamic properties existing in the small volume when the molecular distribution is λ_j. When Eqs. (20) and (22) are substituted into Eqs. (9) and (11), respectively, one obtains an expression for the probability of the transfer of one molecule from the liquid to the vapor at any instant

$$\tau[\lambda_j,\lambda_k]=\frac{k_{LV}\delta A}{\delta t}\exp\left[\left(\frac{\mu^L}{kT^L}-\frac{\mu^V}{kT^V}\right)+\frac{h^V}{k}\left(\frac{1}{T^V}-\frac{1}{T^L}\right)\right] \tag{23}$$

and a probability for the transfer of one molecule from the vapor to the liquid at any instant

$$\tau[\lambda_j,\lambda_i]=\frac{k_{VL}\delta A}{\delta t}\exp\left[-\left(\frac{\mu^L}{kT^L}-\frac{\mu^V}{kT^V}\right)-\frac{h^V}{k}\left(\frac{1}{T^V}-\frac{1}{T^L}\right)\right]. \tag{24}$$

To obtain the expression for the unidirectional evaporation rate, we suppose the intensive properties of the liquid and vapor phases are unchanged during the transfer of ΔN_{LV} molecules. The time required for this transfer is denoted as Δt. Since $\tau[\lambda_j,\lambda_i]$ is constant during this period, we suppose that ΔN_{LV} is proportional to $\tau[\lambda_j,\lambda_i]$ times Δt:

$$\Delta N_{LV}=K_{LV}\exp\left[\left(\frac{\mu^L}{kT^L}-\frac{\mu^V}{kT^V}\right)+\frac{h^V}{k}\left(\frac{1}{T^V}-\frac{1}{T^L}\right)\right]\Delta t, \tag{25}$$

where one finds from Eq. (6) that

$$K_{LV}=C\,\frac{(2\pi)|V_{v\epsilon}|^2\zeta}{\hbar} \tag{26}$$

and C is a proportionality constant. Then in the limit of Δt being small, the unidirectional evaporation flux may be written

$$j^{LV}=K_{LV}\exp\left[\left(\frac{\mu^L}{kT^L}-\frac{\mu^V}{kT^V}\right)+\frac{h^V}{k}\left(\frac{1}{T^V}-\frac{1}{T^L}\right)\right]. \tag{27}$$

In order for Eq. (27) to be valid, the number of molecules transferred during Δt must be very small compared to the number of molecules in each phase:

$$N^\alpha \gg \Delta N_{LV}, \quad \alpha=L \text{ or } V. \tag{28}$$

This condition is examined below. Following a similar procedure, one finds as the expression for the unidirectional condensation rate

$$j^{VL}=K_{VL}\exp\left[-\left(\frac{\mu^L}{kT^L}-\frac{\mu^V}{kT^V}\right)-\frac{h^V}{k}\left(\frac{1}{T^V}-\frac{1}{T^L}\right)\right]. \tag{29}$$

C. Equilibrium exchange rate between the liquid and vapor phases

The small volume and reservoir form an isolated system and the condition for thermodynamic equilibrium is that the total entropy $(S^L+S^V+S^R)$ is a maximum. From this condition, one finds that the necessary conditions for thermodynamic equilibrium are

$$\frac{\mu_e^L}{T_e^L}=\frac{\mu_e^V}{T_e^V}, \quad \frac{1}{T_e^L}=\frac{1}{T_e^V}=\frac{1}{T^L}, \tag{30}$$

where the subscript e on a property indicates that it is to be evaluated at the condition of thermodynamic equilibrium. As the small volume evolves to equilibrium, the vapor phase undergoes a change of temperature and the molecular distribution between the phases is also changed. We assume that K_{LV} and K_{VL} are constant for all molecular distributions and temperatures in this range.

When the small volume and the reservoir have evolved to thermodynamic equilibrium, let the molecular distribution in the volume be denoted as λ_e and the molecular distributions corresponding to the transfer of one molecule from the liquid to the vapor phase and from the vapor to the liquid be denoted as λ_f and λ_d. Following the procedure outlined above, one finds

$$S(\lambda_f)-S(\lambda_e)=\left(\frac{\mu_e^L}{T_e^L}-\frac{\mu_e^V}{T_e^V}\right)+h_e^V\left(\frac{1}{T_e^V}-\frac{1}{T_e^L}\right) \tag{31}$$

and

$$S(\lambda_d)-S(\lambda_e)=-\left(\frac{\mu_e^L}{T_e^L}-\frac{\mu_e^V}{T_e^V}\right)-h_e^V\left(\frac{1}{T_e^V}-\frac{1}{T_e^L}\right). \tag{32}$$

In view of Eq. (30) both $S(\lambda_f)-S(\lambda_e)$ and $S(\lambda_d)-S(\lambda_e)$ vanish and since K_{LV} and K_{VL} have been assumed constant, under equilibrium conditions the expression for the unidirectional rate of evaporation [Eq. (27)] becomes

$$j_e^{LV}=K_{LV} \tag{33}$$

and from Eq. (29)

$$j_e^{VL}=K_{VL}. \tag{34}$$

Under equilibrium conditions, the unidirectional rate of evaporation must be equal to the unidirectional rate of condensation. From Eqs. (33) and (34) one sees that

$$K_{LV}=K_{VL}=K_e, \tag{35}$$

where K_e is the molecular exchange rate between the two phases under equilibrium conditions. Under these conditions, we assume that we may apply classical kinetic theory to determine the rate at which molecules from the vapor phase collide with the liquid-vapor surface and that each of these molecules is transferred to the liquid phase. Thus, if the pressure in the vapor under equilibrium conditions is denoted as P_e^V and the molecular mass as m, then

$$K_e = \frac{P_e^V}{\sqrt{2\pi m k T^L}}. \tag{36}$$

However, under equilibrium conditions, as indicated in Eq. (30), the chemical potential of the molecule in the liquid phase must be equal to that of the molecules in the vapor. For the conditions that we consider

$$\kappa[P^L - P_\infty(T^L)] \ll 1, \tag{37}$$

where κ is the isothermal compressibility and $P_\infty(T^L)$ is the saturation vapor pressure corresponding to the temperature T^L. Thus the liquid phase may be approximated as slightly compressible and the chemical potential may then be written in terms of a reference state. If the reference state is chosen as the saturation condition, then

$$\mu^L(T^L,P_e^L) = \mu[T^L,P_\infty(T^L)] + v_\infty^L[P_e^L - P_\infty(T^L)], \tag{38}$$

where v_∞^L is the specific volume of the saturated liquid phase. If the vapor is approximated as an ideal gas, its chemical potential may also be written in terms of the same reference state

$$\mu^V(T^L,P_e^V) = \mu[T^L,P_\infty(T^L)] + kT^L \ln\left(\frac{P_e^V}{P_\infty}\right). \tag{39}$$

After inserting Eqs. (38) and (39) into Eq. (30), one finds

$$P_e^V = \eta P_\infty(T^L), \tag{40}$$

where

$$\eta = \exp\left(\frac{v_\infty^L}{kT^L}\,[P_e^L - P_\infty(T^L)]\right). \tag{41}$$

Thus K_e may now be expressed

$$K_e = \frac{\eta P_\infty(T^L)}{\sqrt{2\pi m k T}}. \tag{42}$$

In order for Eq. (35) to be valid, the evaporation flux under equilibrium conditions must also be given by Eq. (42).

III. EXPRESSION FOR THE EVAPORATION FLUX

The expression for the net evaporative flux when the system is in molecular distribution λ_j is given by

$$j(\lambda_j) = j^{LV} - j^{VL}. \tag{43}$$

From Eqs. (20), (22), (27), and (35), the net rate of evaporation when the system is in molecular distribution λ_j may be written

$$j(\lambda_j) = \frac{K_e}{\Omega(\lambda_j)}\,[\Omega(\lambda_k) - \Omega(\lambda_i)]. \tag{44}$$

A simple interpretation of this expression may be given: If at a particular instant a certain molecular distribution exists in the small volume, there is a probability for the system to undergo a change in molecular distribution corresponding to evaporation and a probability for the system to undergo a transition corresponding to condensation, but the net rate of change in the molecular distribution is in the direction of the largest number of quantum mechanical states. Under equilibrium conditions, since the entropy is a maximum, the number of quantum mechanical states corresponding to the evaporation of one molecule is equal to the number corresponding to the condensation of one molecule and the unidirectional rates become equal. If the system is displayed from equilibrium, the rate in one direction is enhanced over the equilibrium exchange rate by the ratio of the number of states in the virtual distribution to the number in the instantaneous distribution.

From Eqs. (20), (22), (27), (29), and (43) one finds

$$j(\lambda_j) = K_e\left\{\exp\left[\frac{\mu^L}{T^L} - \frac{\mu^V}{T^V} + h^V\left(\frac{1}{T^V} - \frac{1}{T^L}\right)\right] - \exp\left[-\frac{\mu^L}{T^L} + \frac{\mu^V}{T^V} - h^V\left(\frac{1}{T^V} - \frac{1}{T^L}\right)\right]\right\}, \tag{45}$$

where K_e is given by Eq. (42). Note that this expression for the evaporation flux is in terms of the instantaneous properties of the phases. According to the hypothesis advanced earlier, the values of these properties are the same as those in the steady-state system and in the steady-state system they may be measured [3,4].

A. Expressions for chemical potential and specific enthalpy

In the experimental circumstance of Refs. [3] and [4], the interface between the liquid and vapor phases is curved and the radius of the interface was measured rather than the pressure in the liquid phase. If the liquid surface at a point may be approximated as spherical, the dependence of the evaporation flux on P^L can be replaced by introducing the Laplace equation

$$P^L = P^V + \frac{2\gamma^{LV}}{R_c}, \tag{46}$$

where R_c is the radius of curvature and γ^{LV} is the surface tension. After introducing Eq. (46) into Eq. (38), one finds

$$\frac{\mu^L(T^L,P^L)}{T^L} = \frac{\mu[T^L,P_\infty(T^L)]}{T^L} + \frac{v_\infty^L}{T^L}\left(P^V + \frac{2\gamma^{LV}}{R_c} - P_\infty(T^L)\right). \tag{47}$$

Since the vapor phase has been assumed to behave as an ideal gas, an expression for its chemical potential that is independent of the chemical potential at saturation may be obtained from Boltzmann statistics and the Born-Oppenheimer approximation. It may be expressed in terms of the vibrational, rotational, and electronic partition functions q_{vib}, q_{rot}, and q_{elec}, respectively [14],

$$\frac{\mu^V(T^V,P^V)}{T^V} = -k\ln\left[\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\frac{(kT^V)^{5/2}}{P^V}\right] - k\ln(q_{\mathrm{vib}}q_{\mathrm{rot}}q_{\mathrm{elec}}). \tag{48}$$

The electronic partition function is given by

$$q_{\mathrm{elec}}=g_e \exp\left(\frac{D_e}{kT^V}\right), \tag{49}$$

where g_e and D_e are the degeneracy of the state and the reference potential minimum. The vibrational and the rotational partition functions for the ideal polyatomic molecules may be expressed

$$q_{\mathrm{vib}}=\prod_{l=1}^{n'} \frac{\exp(-\Theta_l/2T^V)}{1-\exp(-\Theta_l/T^V)} \tag{50}$$

and

$$q_{\mathrm{rot}}=\left(\frac{2kT^V}{\hbar^2}\right)^{1.5} \frac{(\pi I)^{0.5}}{\sigma_s}, \tag{51}$$

where Θ_l is a characteristic temperature for vibration, n' is the number of vibrational degrees of freedom, I is the product of principal moments of inertia of the molecule, and σ_s is the symmetry factor of the vibration orientation. For water molecules, the vibrational characteristic temperatures are 3650, 1590, and 3760 K [15] and n' is 3. After subtracting Eq. (48) from Eq. (47) and simplifying, one finds

$$\begin{aligned}\frac{\mu^L(T^L,P^L)}{T^L}-\frac{\mu^V(T^V,P^V)}{T^V}&=\frac{v_\infty^L}{T^L}\left(P^V+\frac{2\gamma^{LV}}{R_c}-P_\infty(T^L)\right)-D_e\left(\frac{1}{T^L}-\frac{1}{T^V}\right)\\&\quad+k\ \ln\left[\left(\frac{T^V}{T^L}\right)^4\left(\frac{P_\infty(T^L)}{P^V}\right)\right]+k\ \ln\left(\frac{q_{\mathrm{vib}}(T^V)}{q_{\mathrm{vib}}(T^L)}\right).\end{aligned} \tag{52}$$

The expression for the enthalpy per molecule of the vapor may also be obtained from the expression for the partition function [14]

$$h^V=4kT^V-D_e+k\sum_{l=1}^{3}\frac{\Theta_l}{2}+k\sum_{l=1}^{3}\frac{\Theta_l}{\exp(\Theta_l/T^V)-1}. \tag{53}$$

Note that these expressions for the chemical potential and the enthalpy are in terms of molecular and material properties T^L, T^V, P^V, and R_c.

B. Expression for fluxes in terms of measurable variables

The expression for the net evaporation flux may now be obtained from Eqs. (27), (29), (42), and (43):

$$j=\frac{\eta P_\infty(T^L)}{\sqrt{2\pi mkT^L}}\left(\exp\frac{\Delta S}{k}-\exp\frac{-\Delta S}{k}\right), \tag{54}$$

where

$$\Delta S=\left(\frac{\mu^L}{T^L}-\frac{\mu^V}{T^V}\right)+h^V\left(\frac{1}{T^V}-\frac{1}{T^L}\right), \tag{55}$$

or from Eqs. (52) and (53)

$$\begin{aligned}\Delta S=k\Bigg\{&4\left(1-\frac{T^V}{T^L}\right)\\&+\left(\frac{1}{T^V}-\frac{1}{T^L}\right)\sum_{l=1}^{3}\left(\frac{\Theta_l}{2}+\frac{\Theta_l}{\exp(\Theta_l/T^V)-1}\right)\\&+\frac{v_\infty^L}{kT^L}\left(P^V+\frac{2\gamma^{LV}}{R_c}-P_\infty(T^L)\right)\\&+\ln\left[\left(\frac{T^V}{T^L}\right)^4\frac{P_\infty(T^L)}{P^V}\right]+\ln\left(\frac{q_{\mathrm{vib}}(T^V)}{q_{\mathrm{vib}}(T^L)}\right)\Bigg\}.\end{aligned} \tag{56}$$

Equation (54) is the final expression for the net evaporation rate. Since it is in terms of experimentally measurable variables, it may be compared with the measurements.

IV. EXAMINATION OF THE SRT EXPRESSION FOR THE EVAPORATION RATE

In Refs. [3] and [4], measurements were made of j,T^L,T^V,P^V,R_c under 5 and 15 separate circumstances, respectively. The theory may be examined by taking all of the parameters except one to be known and then using the theory to predict the value of that parameter. To select the parameter to be predicted, it is important to consider the accuracy with which the variables were measured and the sensitivity of the expression for the net evaporation rate to the independent variables.

A. Available experimental results

1. Experiments of Ref. [3]

In the experimental study of Ref. [3], the temperature was measured near the interface of water as it evaporated under steady-state conditions. Water was pumped into a cylindrical evaporation chamber at an accurately controlled rate with an infusion pump (0.5% accuracy over a liquid flow rate range of 0.48–8.82 l/h). The liquid interface was visible from outside the chamber. The pressure in the evaporation chamber and the flow rate were adjusted to bring the system into a steady state. Once the system had reached a steady state, the temperature in the liquid and in the vapor near the interface on the center line was measured twice, 1 h apart, at each of a series of positions. The maximum deviation in a reading at any position was 0.4% (or 0.7 °C). These measurements were used as the boundary conditions for the continuum energy equation and the temperature at the interface of each phase calculated. The values obtained are listed in Table I. The temperature of water entering the evaporation chamber was near room temperature, but was not controlled. Also the pressure in the vapor was measured with a Pirani-type gauge (Balzers, TPR 018) to an accuracy of approximately ±20%.

The area of the liquid-vapor interface in each experiment was calculated from measured interface parameters and this area was used to determine the net evaporation fluxes. The calculated area of the interface was compared with the image obtained from a charge coupled device camera. Based on measurements 1 h apart, the error was less than 0.1%.

In Fig. 2(a) the temperature measured at the interface in each phase is shown as a function of the measured pressure

TABLE I. Summary of the water evaporation experiments of Ref. [3].

Liquid evaporation rate (μl/h)	Pressure in the vapor (Pa)	Temperature on the vapor side of the interface (±deviation) (°C)	Temperature on the liquid side of the interface (±deviation) (°C)	Radius of interface at center R_c (mm)	Evaporation flux $\bar{j}$ (g m^{-2} s^{-1})
20	1030	13.4±0.1	9.3±0.1	7.02	0.038
30	773	8.5±0.1	3.7±0.1	6.21	0.068
40	546	7.3±0.1	1.9±0.1	6.83	0.119
50	387	4.8±0.1	−3.8±0.1	7.66	0.127
55	293	1.5±0.1	−9.6±0.2	12.04	0.146

in the vapor phase. As may be seen there, the temperature in the vapor was found to be greater than that in the liquid in each experiment case. The average flux was calculated from the measured net evaporation rate and area of the liquid-vapor interface. In Fig. 2(b) the corresponding evaporation rate of each experiment is shown. Note that as the average evaporation flux was increased (by lowering the pressure in the vapor) the temperature discontinuity also increased.

2. *Experiments of Ref. [4]*

In the experimental study of Ref. [4], a procedure similar to that of Ref. [3] was used. There were three notable improvements made in the experimental apparatus. The most important one was in the measurement of the pressure in the vapor phase. The Pirani gauge was replaced with an absolute Hg manometer that could be used to measure the pressure near the liquid-vapor interface with an accuracy of 13.3 Pa (or 0.1 mm). Second, the temperature of the water entering the evaporation chamber was controlled at one of three values, 15 °C, 26 °C, or 35 °C, and at each of these temperatures the flow rate and pressure in the vapor were adjusted until steady-state evaporation was established. The total flow rate of water entering the chamber was measured with the same infusion pump. Third, after a steady state had been reached, the temperature on the center line of the evaporation chamber was measured with two differently sized thermocouples. The measurements made with the smaller thermocouple (25.4 μm in diameter) were used as the boundary conditions for the continuum energy equation and the temperature at the interface of each phase was calculated. This allowed the temperature to be measured closer to the interface than in Ref. [3] and in one case allowed the temperature in the vapor to be measured within one mean free path of the interface. Based on measurements 1 h apart, the maximum temperature difference at the interface in the liquid phase was ±0.2 °C and in the vapor ±0.4 °C. The measured values of T^L, T^V, P^V, R_c, and j for the 15 experiments of Ref. [4] are listed in Table II.

For the experiments of Ref. [4] in which the temperature of the water entering the evaporation chamber was maintained at 35 °C, the temperature in the liquid at the interface, the temperature in the vapor at the interface, and the average evaporation flux are shown in Figs. 3(a) and 3(b) as a function of the measured pressure in the vapor. Note that as a result of replacing the Pirani gauge with the absolute manometer, the pressure in the vapor was much more accurately determined in this case; however, the direction of the temperature discontinuity and the relation between its magnitude and the average evaporation flux is the same as that found in Ref. [3] at each evaporation rate, the temperature at the interface in the vapor is greater than that in the liquid at the interface, and as the evaporation flux was increased the discontinuity in temperature at the interface was observed to increase as well. Similar results were found when water entered the evaporation chamber at 15 °C and 26 °C [4].

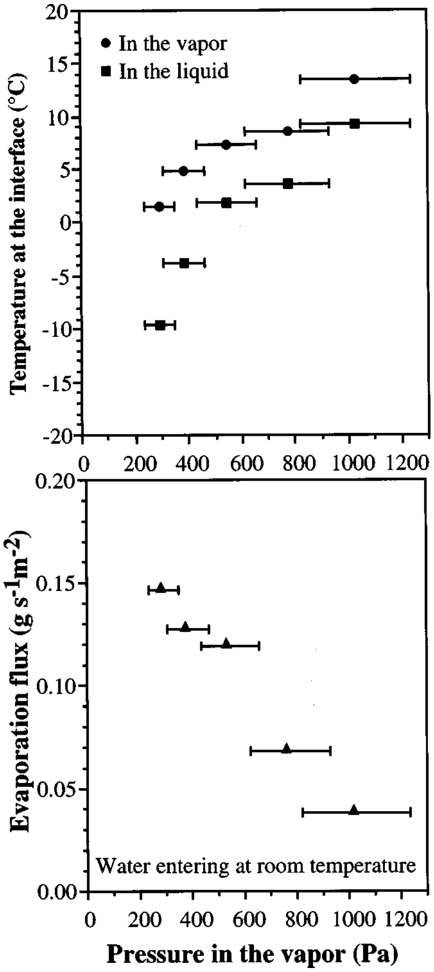

FIG. 2. Summary of the measurements reported in Ref. [3]. The error bars on the pressure indicate possible instrument error.

B. Sensitivity analysis of the evaporation rate expression

The expression for the net evaporation rate [Eq. (54)] may be used to determine the variation in this rate that results

TABLE II. Summary of the water evaporation experiments of Ref. [4].

Liquid evaporation rate (μl/h)	Pressure in the vapor (Pa)	Temperature on the vapor side of the interface (±deviation) (°C)	Temperature on the liquid side of the interface (±deviation) (°C)	Radius of interface at center R_c (mm)	Evaporation flux $\overline{j}$ (g m^{-2} s^{-1})
70[a]	596.0	3.2±0.1	−0.3±0.1	4.42	0.2799
75[b]	493.3	0.6±0.1	−2.9±0.1	4.39	0.2544
85[b]	426.6	−0.6±0.1	−4.8±0.1	4.47	0.3049
90[a]	413.3	−1.0±0.1	−5.2±0.0	4.27	0.4166
100[b]	310.6	−3.8±0.1	−8.9±0.1	3.95	0.3703
100[b]	342.6	−2.7±0.1	−7.7±0.2	4.31	0.3480
100[c]	333.3	−1.6±0.2	−7.8±0.0	4.60	0.3971
110[a]	269.3	−4.6±0.1	−10.7±0.1	4.36	0.4081
110[b]	277.3	−4.3±0.2	−10.3±0.0	4.44	0.4347
120[a]	264.0	−4.9±0.0	−11.0±0.2	4.15	0.4097
120[c]	269.3	−4.1±0.1	−10.6±0.1	4.13	0.4860
130[a]	245.3	−6.0±0.0	−11.9±0.1	4.12	0.4166
140[c]	233.3	−5.2±0.1	−12.4±0.1	4.27	0.4938
150[c]	213.3	−6.2±0.1	−13.5±0.0	4.17	0.5086
160[c]	194.7	−6.8±0.4	−14.6±0.0	4.18	0.5386

[a] The liquid temperature entering the evaporation chamber was 26 °C.
[b] The liquid temperature entering the evaporation chamber was 15 °C.
[c] The liquid temperature entering the evaporation chamber was 35 °C.

from a small change in the independent variables. If the changes in the independent variables are sufficiently small, then

$$\frac{\Delta j}{j}=\frac{1}{j}\left(\frac{\partial j}{\partial P^V}\right)\Delta P^V+\frac{1}{j}\left(\frac{\partial j}{\partial T^L}\right)\Delta T^L+\frac{1}{j}\left(\frac{\partial j}{\partial T^V}\right)\Delta T^V+\left(\frac{\partial j}{\partial R_c}\right)\Delta R_c \tag{57}$$

or

$$\frac{\Delta j}{j}=-\left(\frac{\Delta P^V}{P^V}\right)\coth\left(\frac{\Delta S}{k}\right)-2\,\frac{v_\infty^L\gamma^{LV}}{kT^L}\,\frac{\Delta R_c}{R_c^2}\coth\left(\frac{\Delta S}{k}\right)+\left[\left(\frac{h_{fg}}{kT^L}-\frac{1}{2}\right)+\left(\frac{h_{fg}}{kT^L}-4\right)\coth\left(\frac{\Delta S}{k}\right)\right]\frac{\Delta T^L}{T^L}+\left[4\left(1-\frac{T^V}{T^L}\right)+\frac{1}{T^{V2}}\sum_1^3\frac{\Theta_l\exp(\Theta_l/T^V)}{[\exp(\Theta_l/T^V)-1]^2}\right]\times\frac{\Delta T^V}{T^V}\coth\left(\frac{\Delta S}{k}\right). \tag{58}$$

To estimate the sensitivity of the rate expression to the different parameters, we may consider the experiment with the highest evaporation rate. The quantitative change in the evaporation flux may be calculated from the values of the parameters for this experiment that are listed in Table II,

$$\frac{\Delta j}{j}=-\left(\frac{8.0}{Pa}\right)\Delta P^V-\left(\frac{31.8}{K}\right)\Delta T^L-\left(\frac{0.12}{K}\right)\Delta T^V-\left(\frac{7\times10^{-5}}{m}\right)\Delta R_c. \tag{59}$$

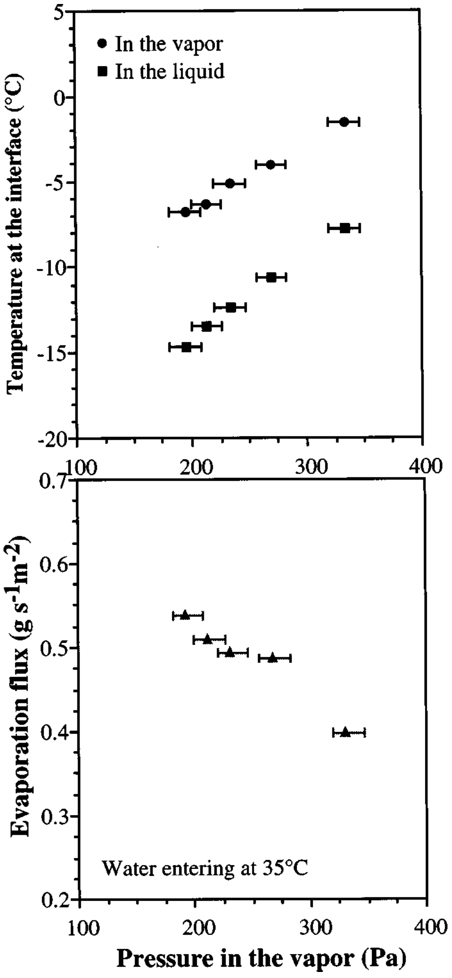

FIG. 3. Summary of the measurements reported in Ref. [4]. The error bars on the pressure indicate the accuracy with which the pressure could be read.

The magnitudes of the coefficients of ΔP^V, ΔT^L, ΔT^V, and ΔR_c are smaller in the expression for $\Delta j/j$ at the lower rates of evaporation.

One of the most accurately measured variables was the net evaporation flux: 0.5%. One of the least accurately measured was the pressure at the interface. If the temperatures T^L, T^V and the radius R_c are taken to have been measured exactly, then in order for the value of the net evaporation flux j to be calculated as accurately as it could be measured, the pressure in the vapor would have to be measured to approximately 6×10^{-4} Pa. However, it was measured to within only ±13.3 Pa in Ref. [4] and to within only 20% of the reading in the experiments of Ref. [3].

If one assumes that P^V, T^V, and R_c were measured exactly, then in order for the net evaporation flux to be calculated as accurately as it could be measured, the temperature at the interface in the liquid would have to be measured to within 1.6×10^{-4} K. It was measured to within only approximately ±0.2 K [3,4]. The error in the measured value of P^V results in an error in the calculated evaporation rate that is two orders of magnitude larger than that from the error in the measured value of T^L.

C. Comparison of the predictions with the measurements

Since the net evaporation rate could be measured more accurately than the other variables, we take the values of j, T^L, T^V, and R_c to be the experimental values listed in Tables I and II and then use the SRT expression for the net evaporation rate to predict the pressure in the vapor P^V that would correspond to these conditions. The predicted and measured pressures obtained by this procedure for the experiments of Refs. [3] and [4] are shown in Figs. 4 and 5. The measured values of the pressure for each net evaporation flux are also shown in these figures and the vertical error bars indicate the accuracy with which the pressure in the vapor was measured.

If the results shown in Fig. 4 alone were considered, one would conclude that there was a small difference in the predictions as compared to the measurements of Ref. [3]. However, when one examines the results shown in Fig. 5, notes that there is no disagreement between the measurements and the predictions at the 15 different experimental conditions reported in Ref. [4], recalls that the pressure was measured closer to the interface and much more accurately in Ref. [4] than in Ref. [3], one concludes that the small difference between the measurements and prediction from the SRT expression for the evaporation flux is not significant. Thus we conclude there is no measured disagreement between the predictions made from the SRT expression and the measurements.

Since the pressure that corresponds to a given evaporation rate is accurately calculated from the SRT expression for the net evaporation flux, even though the measured values of T^L, T^V, R_c are used in the calculations and these variables would be expected to be in error to some degree, the error does not appear significant. However, if measured values of T^L, T^V, R_c, and P^V reported in Ref. [4] are simply inserted in the expression for the evaporation rate, the calculated values of the net evaporation flux could be one order of magnitude larger than the measured value.

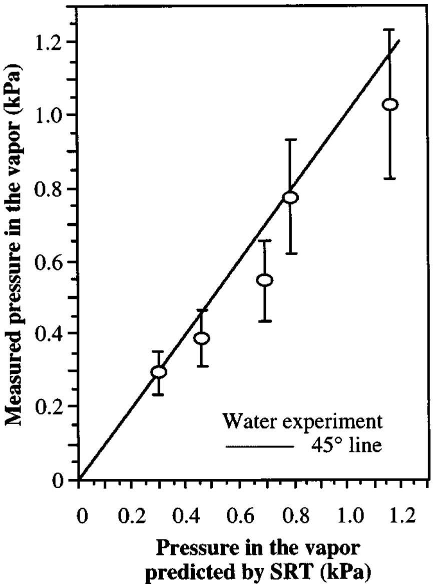

FIG. 4. The SRT expression for the evaporation flux was used to predict the pressure in the vapor phase that would result in a particular evaporation flux if the curvature of the interface and the temperatures in the liquid and in the vapor phase at the interface were those measured [3] and listed in Table I. The predicted values of the pressure are given on the abscissa. The values of the pressure on the ordinate are those measured at the same evaporation flux. If there were perfect agreement, all points would lie on the 45° line. The vertical error bars indicate the uncertainty in the measured value of the pressure.

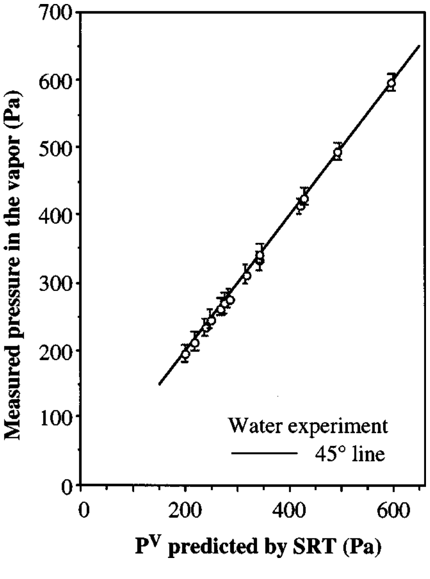

FIG. 5. The SRT expression for the evaporation flux was used to predict the pressure in the vapor phase that would result in a particular evaporation flux if the curvature of the interface and the temperatures in the liquid and in the vapor phase at the interface were those measured [4] and listed in Table II. The predicted values of the pressure are given on the abscissa. The values of the pressure on the ordinate are those measured at the same evaporation flux. If there were perfect agreement, all points would lie on the 45° line. The vertical error bars indicate the uncertainty in the measured values of the pressure and correspond to 13.3 Pa.

V. DISCUSSION AND CONCLUSION

In the SRT procedure, a first-order perturbation theory was used to obtain the expression for the probability of a transition from a quantum mechanical state corresponding to molecular distribution λ_j to a quantum mechanical state of λ_k. A necessary condition for Eq. (7) to be valid is that the time for the transition δt satisfies

$$\delta t \gg \frac{2\pi\hbar}{\Delta E^L + \Delta E^V}. \tag{60}$$

There is also an upper limit to δt. The transition probability and the temperatures and chemical potentials of each phase in the small volume were assumed to be unchanged during Δt when many transitions took place. Thus

$$\Delta t > \delta t \tag{61}$$

and the condition on Δt can be met only if the number of molecules within each phase of the small volume is very large compared to the number of molecules changing phase during Δt. The net number of molecules going from the liquid to the vapor ΔN would be

$$\Delta N = j\,\delta A \Delta t. \tag{62}$$

This number must be very small compared to the number in each phase of the small volume N^α if the thermodynamic properties are to be unchanged:

$$N^\alpha = \frac{\delta A\,\delta L^\alpha}{v^\alpha} \gg \Delta N^\alpha. \tag{63}$$

From Eqs. (60)–(63)

$$\frac{\delta L^\alpha}{v^\alpha j} \gg \delta t \gg \frac{2\pi\hbar}{\Delta E^L + \Delta E^V}. \tag{64}$$

For water ΔE^α may be calculated from Eq. (2):

$$\begin{aligned} \Delta E^L &= 1\times 10^{-20}\ \text{J}, \\ \Delta E^V &= 8\times 10^{-21}\ \text{J}. \end{aligned} \tag{65}$$

The most stringent condition that Eq. (64) must satisfy occurs when the evaporation flux is a maximum

$$\frac{2\times 10^6(\delta L^L)}{m} \gg \delta t s^{-1} \gg 5\times 10^{-14} \tag{66}$$

and for the vapor

$$\frac{3(\delta L^V)}{m} \gg \delta t s^{-1} \gg 8\times 10^{-14}. \tag{67}$$

Since the thermodynamic properties have been assumed uniform over the extent of each phase within the small volume, the value of δL^α could not be any larger than the resolution of the thermodynamic properties. In the vapor phase, this resolution would be approximately one mean free path. The conditions at which the maximum evaporation flux was observed are shown in Table II. At these conditions the mean free path was approximately 25 μm; thus

$$10^{-4} \gg \delta t s^{-1} \gg 8\times 10^{-14}. \tag{68}$$

Based on Eq. (68), it appears that the necessary conditions for the application of the transition probability concept are satisfied.

The sufficient condition for its validity can only be established by comparing the predictions that follow from Eqs. (54) and (56) with experimental results. There are no fitting parameters in the expression for the evaporation rate and as indicated in Fig. 5, at least for water evaporation at low temperature, when the conditions at which the evaporation took place were most accurately measured [4], there is excellent agreement between the predictions and the measurements over a range of experimental conditions. Clearly, other liquids should be examined.

In the SRT approach, the local equilibrium variables are used to determine the expression for the change in entropy resulting from one molecule changing phase. It might be felt that this would limit the validity of the SRT expression for the evaporation flux to ‘‘small’’ values. However, the degree to which the local equilibrium approximation limits the range of rates for which SRT gives a valid expression is not clear. For example, the rate at which water can evaporate is limited because the liquid phase can spontaneously freeze [3]. This possible change in phase of the water limited the rates of evaporation that could be considered experimentally. In addition, as seen in Fig. 5, at least for the water evaporation rates that were achieved, there is no indication that the SRT expression for the evaporation flux is limited to lower evaporation fluxes. Also, when the SRT approach was applied to examine electron transfer reactions [5], gas absorption by liquids [9], adsorption kinetics [10], or thermal desorption kinetics [11], the local equilibrium assumption was used in each case and in each case the SRT approach gave predictions that were in close agreement with measurements over the entire range of rates examined. Thus the limit to the validity of SRT imposed by the local equilibrium assumption is yet to be identified.

Since SRT has led to an expression for the evaporation flux that appears to be in agreement with the measurements of Ref. [4] and the expression has been obtained from the transition probability concepts of quantum mechanics, we investigate the relation of the SRT expression for the evaporation rate with those obtained from the classical kinetic theory approach. Classical kinetic theory does not provide an expression for *predicting* the rate of evaporation. Rather, the kinetic theory expression for the rate is in terms of coefficient(s), but no method is available for predicting these coefficients. However, the classical kinetic theory expressions for the evaporation rate have been used to correlate the results of a number of experiments.

The earlier kinetic theory work assumed that if the liquid were at a temperature T^L, the expression for its unidirectional evaporation flux was the product of the collision frequency of a vapor that had a Maxwellian velocity distribution centered at T^L, a pressure of $P_\infty(T^L)$, and a factor σ_e, the evaporation coefficient. The vapor was also assumed to be in a Maxwellian distribution, but centered at the temperature T^V and with a pressure P^V, and the unidirectional condensation rate was assumed to be a product of the collision frequency of the latter Maxwellian distribution with a coefficient σ_c, the condensation coefficient. These coefficients are usually assumed to have the same value σ^{HK}. Then the Hertz-Knudsen formula [16,17] for the net rate of evaporation may be written [18]

$$j=\frac{\sigma^{\mathrm{HK}}}{\sqrt{2\pi mk}}\left(\frac{P_\infty(T^L)}{\sqrt{T^L}}-\frac{P^V}{\sqrt{T^V}}\right). \tag{69}$$

The Boltzmann equation was not used in the analysis and therefore there was not a necessary relation between T^L, T^V, and P^V.

If the SRT expression for the net evaporation flux [Eq. (54)] is compared with the Hertz-Knudsen expression, the expression for σ^{HK} can be identified. The Hertz-Knudsen expression for the evaporation flux [Eq. (69)] implicitly assumes the liquid-vapor interface is flat. For such an interface, η, given in Eq. (41), has the value unity. Under this condition one finds

$$\sigma^{\mathrm{HK}}=\frac{\exp\left(\frac{\Delta S}{k}\right)-\exp\left(\frac{-\Delta S}{k}\right)}{1-\frac{P^V}{P_\infty(T^L)}\sqrt{\frac{T^L}{T^V}}}. \tag{70}$$

From Eq. (70) and the expression for ΔS given in Eq. (56), SRT indicates that σ^{HK} is a function of the temperature and the pressure in both the liquid and the vapor phases. If Eq. (70) is used to evaluate σ^{HK} from the experimental results reported in Ref. [4] and listed in Table II, one finds that

$$0.060\leqslant\sigma^{\mathrm{HK}}\leqslant 0.133. \tag{71}$$

Many other experiments have indicated that σ^{HK} varies with experimental conditions.

In his analysis of evaporation, Schrage also used classical kinetic theory. He assumed forms of the distribution function, accounted for the bulk velocity of the vapor, and also assumed that there was only one empirical coefficient, which he called the condensation coefficient σ [19]. For small bulk velocities, the expression for the net evaporation rate that he obtained was

$$j=\frac{\sigma}{1-0.5\sigma}\left(\frac{P_\infty(T^L)}{\sqrt{2\pi mkT^L}}-\frac{P^V}{\sqrt{2\pi mkT^V}}\right). \tag{72}$$

The SRT expression for the net evaporation flux may be compared with Eq. (72) and the expression for Schrage's condensation coefficient identified. For a flat liquid-vapor interface one finds

$$\sigma=\frac{\sigma^{\mathrm{HK}}}{1+0.5\sigma^{\mathrm{HK}}}. \tag{73}$$

If one uses Eq. (73), the value of Schrage's condensation coefficient can be evaluated for each of the experiments reported in Ref. [4]. From the data listed in Table II one finds that

$$0.0586\leqslant\sigma\leqslant 0.1247. \tag{74}$$

Values of σ that have been obtained experimentally have been reviewed by Mills and Seban [20]. For water evaporation from a suspended droplet and from a horizontal surface, they record values in the same range as those in Eq. (74). Thus, if one simply used the Hertz-Knudsen or the Schrage expression for the evaporation rate to correlate measurements of the evaporation rate, one would not find any contradictions, only that the coefficients appearing in the expressions for the evaporation rate varied from one experimental circumstance to another.

Subsequent kinetic theory studies of evaporation obtained expressions for the distribution function by solving a model of the Boltzmann equation for the space occupied by the vapor. Different boundary conditions were then imposed. For example, Cipolla, Lang, and Loyalka [2] assumed that the distribution function far from the liquid surface was the Chapman-Enskog distribution and at the liquid surface that the distribution function was a Maxwellian distribution corresponding to the temperature of the liquid at the interface and supposed the number density to be that of a saturated vapor at this temperature. Other boundary conditions were also considered [1,18,21]. All of these more detailed kinetic theory analyses led to the prediction that the liquid could evaporate *only* if the temperature in the vapor was *less* than that in the liquid. This prediction is contrary to the measurements of Refs. [3] and [4]. It is also contrary to the conclusions of SRT. The SRT approach indicates that evaporation can occur when the temperature in the vapor is *greater* than the temperature in the liquid. Indeed, that is the condition existing in all 15 experiments of Ref. [4] and as indicated in Fig. 5, when SRT is applied to predict the pressure at which a particular evaporation rate would be observed for given values of T^L, T^V, R_c, SRT is found to give an accurate prediction of the pressure.

ACKNOWLEDGMENTS

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