## LETTER TO THE EDITOR

Sir:

## Chemical Potential and Nonisothermal Diffusion

Chemical potential is a useful concept in explaining moisture transport under gravitational, capillary, and concentration gradients. It had been hoped that, in addition, it could predict nonisothermal diffusion. An equation was developed and described in Wood Sci. Technol. (1983) 17:101–105 in which this appeared to be the case because of its agreement with preliminary experimental data. The chemical potential term used in this equation was based on the change in heat and free energy in the chemical formation of  $H_2O$  gas. Since this change corresponds to a decrease in entropy, the chemical potential term increases at the rate of approximately 10.7 cal/mol K.

Chris Skaar recently pointed out to me that the chemical potential of both water and  $H_2O$  gas must decrease with increasing temperature, corresponding to the increase in entropy with temperature, with values of approximately -16 and -45cal/mol K respectively. This decrease would predict a movement of moisture from the cool to the warm side in contradiction to experimental results.

An equation developed from the Onsager relationship with a term added to account for the effect of the temperature gradient, as originally presented by Briggs (1967) was proposed in a research note by the author in Wood Sci. (1980) 13(1): 11–13. The thermal heat of transfer term (Q\*) in this equation is assumed to be equal to the activation energy for transverse bound-water diffusion ( $E_b$ ) in the derivation of the modified equation which may be written as:

$$J = -K_{M} \left[ \frac{H}{RT} \left( \frac{\partial M}{\partial H} \right)_{T} \left( \frac{d\mu_{1}^{\circ}}{dT} + \frac{E_{L} + E_{o} + E_{b}}{T} + R \ln Hp_{o} / 7600 \right) \frac{dT}{dx} + \frac{dM}{dx} \right]$$
(1)

where  $d\mu_1^{\circ}/dT$  represents the decrease in the chemical potential of H<sub>2</sub>O gas at 1 atm, H = relative humidity in equilibrium with wood at moisture content M,  $E_L$  = heat of sorption,  $E_o$  = heat of vaporization of water,  $p_o$  = saturated vapor pressure, cm Hg.

The equation may be compared with that developed by Siau (1983), Wood Sci. Technol. 17:101–105.

$$J = -K_{M} \left[ \frac{H}{RT} \left( \frac{\partial M}{\partial H} \right)_{T} \left( \frac{d\mu_{1}^{\circ}}{dT} + \frac{E_{L}}{T} + R \ln H/100 \left( \frac{dT}{dx} + \frac{dM}{dx} \right) \right]$$
(2)

It is fortuitous that both Equations (1) and (2) give nearly identical results and they both agree with nonisothermal experimental results. This is true because the  $d\mu_1^{\circ}/dT$  term of Eq. (1) is approximately -45 cal/mol K,  $(E_o + E_b)/T$  is +63 cal/ mol K, and R ln  $p_o/76$  is -7 cal/mol K for a total of +11 cal/mol K which is very close to the +10.7 cal/mol K, the value of  $d\mu_1^{\circ}/dT$  used in Eq. (2).

To summarize, the new Equation (1) presented here is a correction to Equation (2) proposed in the 1983 paper. It is based on the assumption that the thermal

Wood and Fiber Science, 16(4), 1984, pp. 628–629 © 1984 by the Society of Wood Science and Technology

heat of transfer  $(Q^*)$  is equal to the activation energy for bound-water diffusion. Since the results calculated from both equations are nearly the same, the new equation also predicts nonisothermal diffusion in accordance with our preliminary experiments.

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