

dimers will be greater in the cool regions and smaller in the hot regions, with the dimerization reaction releasing heat and the decomposition reaction absorbing heat as the monomers and dimers circulate, thus increasing the effective rate of heat transfer.

For a gas at its normal boiling temperature and lower, Waelbroeck, Lafleur, and Prigogine (28, 29) applied the thermodynamics of irreversible processes to obtain the heat transferred by the reactive circulation of monomers and dimers, k_r^1 , as follows:

$$k_r^1 = D k_0 \left(\frac{r_{PT}^{(0)}}{k_B T} \right)^2 \frac{n_1 n_2 (n_1 + n_2)}{(n_1 + 2n_2)^2} \quad (9)$$

where n_1 and n_2 are the molecular concentrations of monomer and dimer, respectively, D is the diffusion coefficient, and $r_{PT}^{(0)}$ is the heat of the dissociation reaction. The authors estimated that for argon at its boiling temperature, k_r^1 contributes about 6% to the thermal conductivity.

At higher temperatures and at low pressures, the concentration of dimer is small. However, near the critical point the concentrations of dimer and much larger clusters become significant, thus accounting for the large increase in the conductivity at temperatures close to the critical temperature and at densities near the critical density.