

# From the Arrhenius to the Clausius–Clapeyron Equation

Igor Novak

Department of Chemistry, Faculty of Science, National University of Singapore, Singapore 117543, Singapore, [chmigorn@nus.edu.sg](mailto:chmigorn@nus.edu.sg)

Received June 10, 2002. Accepted August 25, 2002.

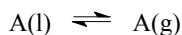
**Abstract:** The dynamical nature of chemical equilibrium and the relationship between kinetics and thermodynamics are illustrated by the example of a pure liquid that is in equilibrium with its vapor.

## Introduction

The topics of chemical equilibrium and reaction rates are fundamental concepts in chemistry. The behavior of a pure liquid in equilibrium with its vapor is described by the Clausius–Clapeyron equation and the rates of chemical reactions are described by the Arrhenius equation. In this work we draw educationally useful parallels between the two equations and also between kinetics and thermodynamics. The approach outlined uses elementary mathematics and is suitable for freshmen studying general chemistry or as a review for second-year students studying physical chemistry.

## Discussion

The pure liquid is in equilibrium with its vapor in a closed vessel (fixed volume and temperature; the vapor behaves ideally).



The standard derivation of the dependence of the vapor pressure,  $P$ , on temperature,  $T$ , uses either classical thermodynamic relationships between state functions or the Boltzmann distribution [1]. The latter approach requires a previous understanding of statistical mechanics. This approach requires only an elementary understanding of chemical kinetics and equilibrium. For the equilibrium between a pure liquid and its vapor, the equilibrium constant,  $K$ , is a ratio of the rate constants for the two opposing processes: evaporation,  $k_v$ , and condensation,  $k_c$ , that is,  $K = k_v/k_c$ . The rates of the two processes can be written using the Arrhenius equation [2–4] as follows.

$$\ln k_v = \ln A_v - \frac{E_{a,v}}{RT} \quad (1)$$

$$\ln k_c = \ln A_c - \frac{E_{a,c}}{RT} \quad (2)$$

Combining eqs 1 and 2 gives

$$\ln k_v - \ln k_c = \ln K = \ln A_v - \ln A_c - \frac{(E_{a,v} - E_{a,c})}{RT} \quad (3)$$

The term  $(\ln A_v - \ln A_c)$  is constant because  $A$  factors are constant (as required by the Arrhenius equation), so are their logarithms, and thus the difference between the logarithms is constant as well.

The  $(E_{a,v} - E_{a,c})$  term can be expressed in term of internal energies as  $E_{a,v} = U^\ddagger - U_v$  and  $E_{a,c} = U^\ddagger - U_c$ , where  $U^\ddagger$  is the internal energy for the transition state in going from the liquid to vapor or vice versa. The difference in activation energies between the phases then becomes  $\Delta U = U_c - U_v$ . Also, from the definition of enthalpy we have  $U_c = H_c$  and  $U_v = H_v - (PV)_v$ , so

$$E_{a,v} - E_{a,c} = \Delta U = H_c - H_v + (PV)_v \quad (4)$$

The first two terms in eq 4 represent the enthalpy of vaporization, that is,  $\Delta H_{\text{vap}} = H_c - H_v$ . The third term, the work term, is constant because of the assumed ideal gas behavior of the vapor and constant  $P$  and  $T$  in the system:  $(PV)_v = nRT$ . The work term when introduced into eq 3 gives another constant term. Equation 3 can therefore be written as

$$\ln K = C_1 - \Delta H_{\text{vap}}/(RT)$$

Because  $K$  is proportional to the vapor pressure,  $P$ ,  $\ln K = \ln P + C_2$ . Combining the two equations we get

$$\ln P = (C_1 - C_2) - \Delta H_{\text{vap}}/(RT) = C - \Delta H_{\text{vap}}/(RT)$$

which is the Clausius–Clapeyron equation.

The important insight here is not just the demonstration of the link between kinetics and equilibrium, but also a simple observation about how the presence of interactions between the particles leads to the nonlinear behavior of the system. This can be demonstrated as follows. In the ideal gas system the pressure responds linearly to temperature changes, that is,  $PV = nRT$ , however, in the liquid/vapor system discussed above the response of system pressure to temperature changes is nonlinear (logarithmic) as the Clausius–Clapeyron equation indicates. The difference in behavior is obviously due to the interactions between the particles in the liquid. Such interactions are indeed necessary to hold the liquid together. This insight may be important for understanding how the multitude of interactions present in biological systems causes them to respond nonlinearly to external stimuli. It is this nonlinearity that leads to biodiversity and the adaptability of biological systems.

**Acknowledgment.** The author wishes to thank an anonymous referee for very useful suggestions to improve this manuscript.

#### References and Notes

1. Castellan, G. W. *Physical Chemistry*, 3rd ed.; Addison-Wesley: Reading, MA, 1983.
2. Levine, I. N., *Physical Chemistry* 5th ed.; McGraw-Hill: New York, 2002.
3. Laidler, K. J. *J.Chem.Educ.* **1984**, 61, 495.
4. Logan, S. R. *J.Chem.Educ.* **1982**, 59, 279.