

The concealed truth behind equilibrium

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Relation between equilibrium and temperature is investigated. The assumption of ideal-gas behavior and invariability of $\Delta_r H_m$ is verified and help achieve great linearity of $\ln p$ or $\ln K^\ominus$ towards $1/T$. Machine learning method is utilized to apply Antoine method, which fails to give satisfying results.

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and that

$$dn_r = -k_r dn, \quad dn_p = k_p dn \quad (4)$$

where r stands for reactants and p for products, and k refers to the coefficient of the matter assigned in the chemical reaction. Thus K is defined as

$$K = \prod_B p_B^{k_B} \quad (5)$$

and

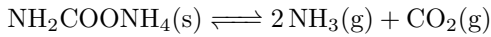
$$K^\ominus = \left(\frac{p_B}{p^\ominus} \right)^{k_B} \quad (6)$$

with reference to the standard state. Thus

$$\Delta_r G_m^\ominus = -RT \ln K^\ominus \quad (7)$$

I. INTRODUCTION

Ammonium carbamate, being an intermediate for the synthesis of urea, is remarkable due to its ability to decompose,



It is a perfect approximation that the chemical potential of a solid substance is constant, which leads to the obvious conclusion that the reaction is dominated by the chemical potential of the gases produced. Regarding them as ideal gases, we get the chemical potential of them,

$$\mu_B = \left(\frac{\partial G}{\partial n_B} \right)_{p,T,n_C} = RT \ln p_B \quad (1)$$

w.r.t. the Gibbs free energy of an ideal gas,

$$dG_{\text{ideal}} = V dp \Big|_{dT=0} = \frac{nRT}{p} dp \Big|_{dT=0} = nRT d \ln p \Big|_{dT=0} \quad (2)$$

and the assumption that there is no interaction among ideal gases.

When a reaction reaches its equilibrium, it follows

$$dG = 0 \Rightarrow \Delta_r G_m dn + \sum_B \mu_B dn = 0 \quad (3)$$

$$-RT \ln K = \Delta_r G_m = \Delta_r H_m - T \Delta_r S_m \quad (8)$$

$$\ln K = -\frac{\Delta_r H_m^\ominus}{RT} + \frac{\Delta_r S_m}{R} \quad (9)$$

It is assumed that $\Delta_r H_m$ as well as $\Delta_r S_m$ does not vary with temperature, then

$$\frac{d \ln K}{dT} = \frac{\Delta_r H_m^\ominus}{RT^2} \quad (10)$$

After integration, we obtain

$$\ln K = -\frac{\Delta_r H_m^\ominus}{RT} + \text{constant} \quad (11)$$

Vaporization is another kind of equilibrium, namely the equilibrium between liquid phase and gas phase. During vaporization the temperature remains constant, and it is assumed that $\Delta_{\text{vap}} H_m^\ominus$ is constant, thus

$$RT d \ln p_B = d\mu_B = S_m dT = \frac{\Delta_{\text{vap}} H_m}{T} dT \quad (12)$$

then

$$\frac{d \ln p_B}{dT} = \frac{\Delta_{\text{vap}} H_m}{RT^2} \quad (13)$$

After integration, we obtain

$$\ln p_B = -\frac{\Delta_{\text{vap}} H_m}{RT} + \text{constant} \quad (14)$$

When the gases does not completely follow the behaviors of ideal gases, deviation will occur. To fix this, perturbation factors can be added, such as expanding it in a series of T , namely

$$P(T) = k \sum_n a_n T^{-n} \quad (15)$$

If we assume that $a_n = C^n$ for $n \geq 2$, where C is a constant, it can be summed to give

$$P(T) = \frac{1}{1 - \left(\frac{C}{T}\right)} - 1 = \frac{C}{T - C} \quad (16)$$

Combining it with 14, Antoine equation can be deduced,

$$\ln p = A - \frac{B}{T - C} \quad (17)$$

II. METHODS AND PROCEDURES

A. Measurement of saturated vapor pressure of water

Deionized water is stored in a container with good gas tightness and connected to atmosphere *via* a capillary with a valve. The container is vacuated and the water is heated by an electric heating wire to keep boiling vigorously. The temperature of water is measured using Pt thermometer, while the pressure is measured using digital pressure measurement device. A series of data at different pressure is obtained by leaking some gas into the apparatus through adjusting the valve.

B. Measurment of decomposition equilibrium constant of ammonium carbamate

The system consists of a small bulb containing ammonium carbamate connected to a U-shaped trap containing silicone oil, a thermostat that keeps the bulb at a constant temperature, a digital pressure measurement device that measures the pressure of the system, capillary with a valve that connects the system to atmosphere, and a bottle to buffer the leaking of the gas so that small change of pressure can be achieved. The apparatus is vacuated until the pressure remains constant for few minutes. a series of data is collected by adjusting the temperature set in the thermostat and wait for the ammonium carbamate to reach chemical equilibrium with ammonia and carbon dioxide in gas phase, during which appropriate amount of gas is added into the system by adjusting the valve to keep the surfaces of the oil paralleled to the ground. Notably, the system at 25 °C is experimented twice to verify the reliability of the results.

TABLE I. Data collected in the measurement of the saturated vapor pressure of water

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
344.38	31.62	345.83	33.77	347.20	35.86
349.22	39.17	351.06	42.44	352.79	45.71
355.31	50.79	356.92	54.62	358.82	58.92
360.85	63.98	363.93	72.11	365.27	75.89
366.79	80.50	368.95	87.33	371.05	93.09

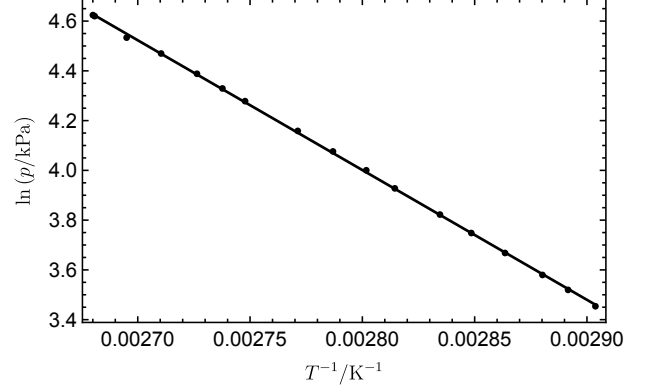


FIG. 1. Data of the saturated vapor pressure of water fitted by $\ln p - \frac{1}{T}$ curve

III. RESULT AND ANALYSIS

A. Measurement of saturated vapor pressure of water

The data recorded is shown in Table.I. The data is fitted using Clausius method and Antoine method respectively, as shown in Fig.1. The line fitted is

$$\ln(p/\text{kPa}) = -5217 \times \frac{1}{T/\text{K}} + 18.61 \quad (18)$$

with $R^2 = 0.999788$. Thus $\Delta_{\text{vap}} H_m^\ominus$ can be deduced, w.r.t. the fact that Δ_{vap} is assumed to be irrelevant with

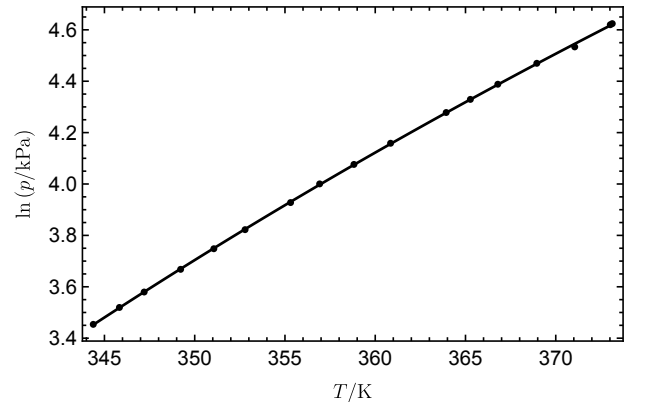


FIG. 2. Data of the saturated vapor pressure of water fitted using Antoine method

temperature,

$$\Delta_{\text{vap}}H_m^\ominus = 5278 \text{ K} \times R = 43.37 \text{ kJ/mol} \quad (19)$$

which is close to that given in the reference (44.00 kJ/mol[1]), verifying the deductions as well as assumptions given for the Clausius method. Deviation may arise from measurement error both during measuring temperature and pressure. Slight difference of temperature over the water during heating might also contribute to it by invalidating the invariability of $\Delta_{\text{vap}}H_m$, while deviation from equilibrium of pressure can also affect the result. It may also be considered that the water vapor may not completely follow the behaviors of an ideal gas, which makes the Clausius method does not give the explicit result. Further, the heat capacity of water changes at different temperature, which deviates Δ_{vap} from that in standard state.

$$\Delta_{\text{vap}}H_m^\ominus = 5278 \text{ K} \times R = 43.88 \text{ kJ/mol} \quad (20)$$

Machine learning integrated in *Mathematica* returns the result in Antoine method, namely

$$\ln(p/\text{kPa}) = A - \frac{B}{T - C}, \quad \begin{cases} A = 13.62, \\ B = 2250, \\ C = 123.1 \end{cases} \quad (21)$$

Thus

$$\Delta_{\text{vap}}H_m^\ominus = 54.24 \text{ kJ/mol}, \Delta_{\text{vap}}S_m^\ominus = 181.9 \text{ J/(mol} \cdot \text{K)} \quad (22)$$

both of which does not match the data from reference. This might be due to the deficiency of accuracy describing the deviation in Antoine method, which simply treat the deviation as geometric series of $1/T$. It might also be due to inaccuracy in machine learning, whose complicated deduction of parameters may easily result in phenomena called ‘overfitting’. However, simple penalty function by introducing the norm of the parameters did not completely solve this problem, indicating a serious issue in this method.

B. Measurement of decomposition equilibrium constant of ammonium carbamate

The data recorded is shown in Table.II. The line fitted is

$$\ln(p/\text{kPa}) = -6491 \times \frac{1}{T/\text{K}} + 24.23 \quad (23)$$

with $R^2 = 0.999795$. Considering that

$$p_{\text{CO}_2} = \frac{1}{3}p_{\text{total}}, p_{\text{NH}_3} = \frac{2}{3}p_{\text{total}} \quad (24)$$

it is easily deduced that

$$\ln K^\ominus = 3 \ln p + \text{constant} \quad (25)$$

TABLE II. Data collected in the measurment of decomposition equilibrium constant of ammonium carbamate

T/K	p/kPa
298.15	11.63
303.15	16.91
308.15	23.89
313.15	33.46
318.16	45.74

thus

$$\Delta_r H_m^\ominus = 161.9 \text{ kJ/mol} \quad (26)$$

Unfortunately, data from references cannot be searched. Great linearity is achieved, verifying the model provided for this reaction. Sources of deviations resembles the experiment in the measurement of saturated vapor pressure of water, including the non-ideal-gas behavior, failure to reach the chemical equilibrium, as well as measurement error.

IV. CONCLUSIONS

From the equations and the experiment results we observe an intimate relation between equilibrium and temperature, which is due to the sophisticated connection between energy and entropy. Assumption of ideal-gas behavior in the gas phase of the products as well as the indifference of deviation of $\Delta_r H_m$ towards temperature leads to linearity of $\ln p$ or $\ln K$ towards $\frac{1}{T}$, which is successfully verified by experiments.

[1] E. Franck, Berichte der Bunsengesellschaft für physikalische Chemie **94**, 93 (1990).