Three-Step Reversible Cycle

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1 Introduction

In a posting to the CHEMED-L chemical education listserv on 1 August 2003, Pentcho Valev claims to have discovered an exception to the Clausius inequality.

Pentcho's example is that of a closed system ontaining liquid and gaseous phases of a pure substance in phase equilibrium. The system undergoes a cycle of three reversible steps:

1. adiabatic expansion resulting in vaporization and cooling;
2. heating at constant volume until the initial temperature is regained;
3. compression at constant temperature and pressure until the initial state is reached.

Pentcho claims that if the molar enthalpy of vaporization is large, the integral of $\mathrm{d}q/T$ for the cycle can be positive; whereas the Clausius inequality predicts the integral must be zero (because for reversible steps it equals the net entropy change).

I carried out calculations based on high-accuracy experimental data for water available from the U.S. National Institute of Standards and Technology (NIST). These calculations showed that the cyclic integral $\oint \mathrm{d}q/T$ for Pentcho's cycle is *zero*, contrary to his claim and in agreement with the Clausius inequality for a cycle of reversible steps.

2 Symbols

n	total amount (moles) of H_2O – a constant
n_l	amount (moles) of liquid
n_g	amount (moles) of gas
q, w	heat, work
T, p, V	temperature, pressure, volume
U, H	(internal) energy, enthalpy
$V_\mathrm{m}(\mathrm{l})$, $V_\mathrm{m}(\mathrm{g})$	molar volumes of liquid and gas
$H_\mathrm{m}(\mathrm{l})$, $H_\mathrm{m}(\mathrm{g})$	molar enthalpies of liquid and gas
$\Delta_\mathrm{vap}V_\mathrm{m}$	molar volume of vaporization
$\Delta_\mathrm{vap}H_\mathrm{m}$	molar enthalpy of vaporization
F	$\mathrm{d}p/\mathrm{d}T$ along the liquid-gas coexistence curve

3 Mathematical Relations

3.1 General relations

The amounts are related by $n = n_\mathrm{l} + n_\mathrm{g}$, with n constant, giving

$$n_\mathrm{l} = n - n_\mathrm{g} \qquad \mathrm{d}n_\mathrm{l} = -\mathrm{d}n_\mathrm{g}$$

Since the changes in the cycle are reversible, the system is regarded as being in an equilibrium state at all times, with uniform T and p and the liquid and gas in phase equilibrium. Then p (equal to the vapor pressure of the liquid) is a function of T only. Infinitesimal changes in p and T along the liquid–gas coexistence curve are related by the Clapeyron equation $\mathrm{d}p/\mathrm{d}T = F$ where the function F is given by

$$F = \frac{\Delta_\mathrm{vap} H_\mathrm{m}}{T \Delta_\mathrm{vap} V_\mathrm{m}} \tag{1}$$

Normally the intensive properties of a pure phase, such as $V_\mathrm{m}(\mathrm{l})$, are functions of p and T. When p is a function of T, however, the intensive properties, including $\Delta_\mathrm{vap} V_\mathrm{m}$ and $\Delta_\mathrm{vap} H_\mathrm{m}$, are functions of T only.

The system has two independent variables. The total differentials of V and H, with T and n_g as the independent variables, are given by

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_{n_\mathrm{g}} \mathrm{d}T + \left(\frac{\partial V}{\partial n_\mathrm{g}}\right)_T \mathrm{d}n_\mathrm{g}$$

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_{n_\mathrm{g}} \mathrm{d}T + \left(\frac{\partial H}{\partial n_\mathrm{g}}\right)_T \mathrm{d}n_\mathrm{g}$$

The partial derivatives $(\partial V/\partial n_\mathrm{g})_T$ and $(\partial H/\partial n_\mathrm{g})_T$ are equal to $\Delta_\mathrm{vap} V_\mathrm{m}$ and $\Delta_\mathrm{vap} H_\mathrm{m}$, respectively, so the previous equations become

$$\mathrm{d}V = \left(\frac{\partial V}{\partial T}\right)_{n_\mathrm{g}} \mathrm{d}T + \Delta_\mathrm{vap} V_\mathrm{m}\,\mathrm{d}n_\mathrm{g} \tag{2}$$

$$\mathrm{d}H = \left(\frac{\partial H}{\partial T}\right)_{n_\mathrm{g}} \mathrm{d}T + \Delta_\mathrm{vap} H_\mathrm{m}\,\mathrm{d}n_\mathrm{g} \tag{3}$$

3.2 Step 1

Step 1 is adiabatic: $\mathrm{d}q = 0$. The first law applied to Step 1 is

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w = 0 - p\,\mathrm{d}V$$

The infinitesimal enthalpy change is

$$\mathrm{d}H = \mathrm{d}(U + pV) = -p\,\mathrm{d}V + p\,\mathrm{d}V + V\,\mathrm{d}p = V\,\mathrm{d}p = VF\mathrm{d}T \tag{4}$$

Equating the expressions for $\mathrm{d}H$ in Equations 3 and 4 gives

$$\left(\frac{\partial H}{\partial T}\right)_{n_\mathrm{g}} \mathrm{d}T + \Delta_\mathrm{vap}H_\mathrm{m}\,\mathrm{d}n_\mathrm{g} = VF\,\mathrm{d}T$$

or

$$\mathrm{d}n_\mathrm{g} = \frac{VF - (\partial H/\partial T)_{n_\mathrm{g}}}{\Delta_\mathrm{vap}H_\mathrm{m}}\,\mathrm{d}T \tag{5}$$

Combining Equations 1, 2, and 5 gives

$$\mathrm{d}V = \left[\left(\frac{\partial V}{\partial T}\right)_{n_\mathrm{g}} + \frac{V}{T} - \frac{1}{FT}\left(\frac{\partial H}{\partial T}\right)_{n_\mathrm{g}}\right]\mathrm{d}T \tag{6}$$

3.3 Step 2

The volume is constant in Step 2: $\mathrm{d}V = 0$. Equation 2 becomes

$$0 = \left(\frac{\partial V}{\partial T}\right)_{n_\mathrm{g}} \mathrm{d}T + \Delta_\mathrm{vap}V_\mathrm{m}\,\mathrm{d}n_\mathrm{g}$$

or

$$\mathrm{d}n_\mathrm{g} = -\frac{(\partial V/\partial T)_{n_\mathrm{g}}}{\Delta_\mathrm{vap}V_\mathrm{m}}\,\mathrm{d}T \tag{7}$$

The energy change is $\mathrm{d}U = \mathrm{d}q + \mathrm{d}w = \mathrm{d}q + 0$, and the enthalpy change is

$$\mathrm{d}H = \mathrm{d}(U + pV) = \mathrm{d}q + V\mathrm{d}p = \mathrm{d}q + VF\,\mathrm{d}T \tag{8}$$

Equating the expressions for $\mathrm{d}H$ in Equations 3 and 8, making substitutions from Equations 1 and 7, and rearranging gives

$$\mathrm{d}q = \left[\left(\frac{\partial H}{\partial T}\right)_{n_\mathrm{g}} - FT\left(\frac{\partial V}{\partial T}\right)_{n_\mathrm{g}} - VF\right]\mathrm{d}T \tag{9}$$

4 Calculations

The calculations were made with a program written in Pascal, using experimental data for water downloaded from the NIST Chemistry WebBook at `webbook.nist.gov`. The data used were values of p, $V_\mathrm{m}(\mathrm{l})$, $V_\mathrm{m}(\mathrm{g})$, $H_\mathrm{m}(\mathrm{l})$, and $H_\mathrm{m}(\mathrm{g})$, tabulated at a temperature increment of 0.25 K along the liquid-gas coexistence curve.

4.1 Integration

The integrations referred to in the following paragraphs were carried out as numerical integrations over temperature with a temperature increment or decrement of 0.25 K and using the trapezoidal rule. The integrands of the integrals required values of various quantities evaluated as follows.

At a given temperature, the molar volumes and enthalpies of vaporization were calculated from

$$\Delta_{\mathrm{vap}} V_{\mathrm{m}} = V_{\mathrm{m}}(\mathrm{g}) - V_{\mathrm{m}}(\mathrm{l}) \qquad \Delta_{\mathrm{vap}} H_{\mathrm{m}} = H_{\mathrm{m}}(\mathrm{g}) - H_{\mathrm{m}}(\mathrm{l})$$

At a given temperature and for a given value of n_{g}, the volume and enthalpy were found from

$$V = n_{\mathrm{l}} V_{\mathrm{m}}(\mathrm{l}) + n_{\mathrm{g}} V_{\mathrm{m}}(\mathrm{g}) \qquad H = n_{\mathrm{l}} H_{\mathrm{m}}(\mathrm{l}) + n_{\mathrm{g}} H_{\mathrm{m}}(\mathrm{g})$$

The partial derivatives $(\partial V/\partial T)_{n_{\mathrm{g}}}$ and $(\partial H/\partial T)_{n_{\mathrm{g}}}$ were evaluated, at a given value of T and of n_{g}, as the averages of $\Delta V/\Delta T$ and $\Delta H/\Delta T$ in the two adjacent temperature intervals while keeping n_{l} and n_{g} constant.

4.2 Calculations for one cycle

The calculations for a particular three-step cycle were made with specified values of the total amount of water n, the initial amount of gas, and the initial and final temperatures in Step 1.

For Step 1, n_{g} after each temperature decrement was found by integrating Equation 5. The volume change in Step 1 was found by integrating Equation 6, and the work was calculated as $-\int p\,\mathrm{d}V$ with $\mathrm{d}V$ given by Equation 6.

For Step 2, integration of Equation 7 was used to find n_{g} after each temperature increment. Equation 9 was used to evaluate q and $\int \mathrm{d}q/T$.

In Step 3, taking place at constant T and p, the work is $-p\Delta V$. The heat is $q = \Delta n_{\mathrm{g}} \Delta_{\mathrm{vap}} H_{\mathrm{m}}$ (where Δn_{g} is the negative of the changes of n_{g} in Steps 1 and 2), and $\int \mathrm{d}q/T$ is equal to q/T.

5 Results

The calculated values listed below are for a cycle in which the total amount of water is $n = 10\,\mathrm{mol}$, the water is initially all in the liquid phase, and the temperature in Step 1 changes from 350.00 K to 325.00 K.

	T (K)	p (kPa)	V (m^3)	n_{g} (mol)
initially	350.00	41.682	1.8502×10^{-4}	0
after Step 1	325.00	13.531	8.4535×10^{-2}	0.42420
after Step 2	350.00	41.682	8.4535×10^{-2}	1.21903

	q (kJ)	w (kJ)	$\int \mathrm{d}q/T$ (J/K)
Step 1	0	-1.8319	0
Step 2	49.177	0	145.32
Step 3	-50.860	3.5159	-145.31

The important thing to note is that, within the precision of the calculation, the cyclic integral $\oint \mathrm{d}q/T$ (the sum of the values in the last column of the second table) is *zero*.