

**A LOWER LIMIT ΔH_{vap}^Z FOR THE LATENT HEAT OF
VAPORIZATION ΔH_{vap} WITH RESPECT TO THE PRESSURE
AND THE VOLUME CHANGE OF THE PHASE TRANSITION.**

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ABSTRACT. We derive a lower limit ΔH_{vap}^Z for the latent heat of vaporization ΔH_{vap} with respect to the pressure and the volume change of the phase transition from the study of a heat engine using liquid-gas as working fluid with an infinitesimal variation of the temperature δT and an infinitesimal variation of the pressure δP and in the vanishing limit of the massive flow rate Q_m . We calculate the latent heat index $h^Z = \Delta H_{vap}^Z / \Delta H_{vap}$ of few gas and at few different pressures P . Finally, we consider the latent heat index limit h_{cr}^Z as the temperature T approaches the critical temperature T_{cr} .

We derive a lower limit expression for the latent heat of vaporization ΔH_{vap} from the study of a heat engine using liquid-gas as working fluid with an infinitesimal variation of the temperature δT and an infinitesimal variation of the pressure δP and in the vanishing limit of the massive flow rate Q_m :

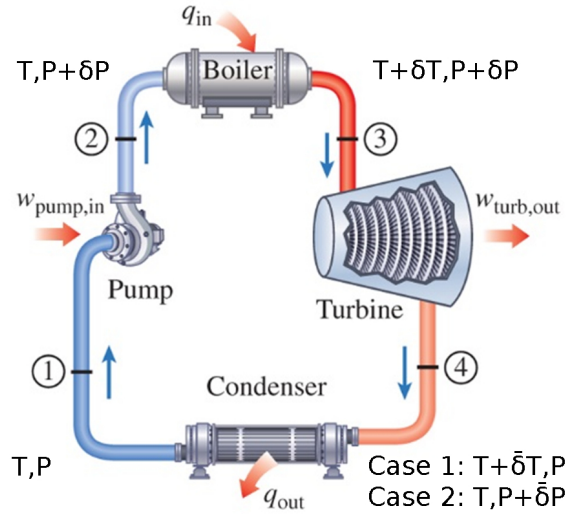


FIGURE 1. Heat engine with $\bar{\delta}T < \delta T$ and $\bar{\delta}P < \delta P$.

Case: 2: $\bar{\delta}P = 0$

With infinitesimal variations of the temperature and infinitesimal variations of the volume and a vanishing limit of the massive flow rate Q_m , the irreversible processes

Date: January 6, 2021.

are negligible and the efficiency of that heat engine is maximal:

$$\eta = 1 - \frac{T}{T+\delta T} = \frac{\delta T}{T} + \mathcal{O}(\delta^2 T)$$

The input power of that heat engine is: $P_{in} = Q_m \Delta H_{vap} + \mathcal{O}(\delta P)$.

The output power of that heat engine is: $P_{out} = Q_m \nu \delta P$ where ν is the specific volume of the gas.

Therefore, we derive the efficiency of that heat engine in a second way:

$$\eta = \frac{P_{out}}{P_{in}} = \frac{\nu \delta P}{\Delta H_{vap}} + \mathcal{O}(\delta^2 P)$$

Finally the case 1 is impossible since it breaks the well known Clausius–Clapeyron relation:

$$\frac{\delta P}{\delta T} = \frac{\Delta H_{vap}}{T(\nu - \nu_l)} \neq \frac{\Delta H_{vap}}{T\nu}$$

Case: 1: $\bar{\delta T} = 0$

We start from $\bar{\delta P} < \delta P$:

$$1 > \frac{\bar{\delta P}}{\delta P} = \frac{\delta T}{\delta P} \frac{\bar{\delta P}}{\delta T} = \frac{T(\nu - \nu_l)}{\Delta H_{vap}} \frac{\bar{\delta P}}{\delta T}$$

From there, we express $\frac{\bar{\delta P}}{\delta T}$ with respect to $\frac{\delta V}{\delta P}$ with the help of the following equation of state:

$$\begin{aligned} \delta V &= \left(\frac{\partial V}{\partial T}\right)_P \delta T + \left(\frac{\partial V}{\partial P}\right)_T \bar{\delta P} = V(\alpha \delta T - \beta_T \bar{\delta P}) \\ \frac{\bar{\delta P}}{\delta T} &= \frac{P\alpha}{V \frac{\delta V}{\delta P} + P\beta_T} \\ \frac{\bar{\delta P}}{\delta T} &= \frac{P}{T} \frac{\gamma_a T \alpha}{\gamma_a P \beta_T - 1} \end{aligned}$$

, where γ_a is the adiabatic index such that $V \bar{\delta P} = -\gamma_a P \delta V$.

Finally, we derive a lower limit expression for the latent heat of vaporization ΔH_{vap} :

$$\Delta H_{vap}^Z = \frac{\gamma_a T \alpha}{\gamma_a P \beta_T - 1} P(\nu - \nu_l) = \frac{\gamma_a T \alpha}{\gamma_a P \beta_T - 1} P(\nu - \nu_l) < \Delta H_{vap}$$

We can define some latent heat index h^Z ranging between 0 and 1:

$$h^Z = \frac{\Delta H_{vap}^Z}{\Delta H_{vap}} = \frac{\gamma_a T \alpha}{\gamma_a P \beta_T - 1} \frac{P(\nu - \nu_l)}{\Delta H_{vap}} = \frac{\gamma_a T \alpha}{\gamma_a P \beta_T - 1} \frac{P}{T} \frac{dT}{dP} < 1$$

From the above equation and the definition of an adiabatic expansion:

$$\frac{dV}{V} = \alpha dT - \beta_T dP \quad \text{and} \quad -P \frac{dV}{V} = (c_P - P\alpha) dT + (P\beta_T - T\alpha) dP$$

, we derive an expression for the adiabatic index γ_a with respect to the heat capacity ratio γ :

$$\gamma_a = -\frac{P}{V} \frac{dV}{P} = \frac{1}{P\beta_T - \frac{P}{c_p} T\alpha^2} = \frac{\gamma}{P\beta_T}$$

To conclude the theoretical part, we develop γ_a with respect to the heat capacity ratio γ inside the previous results:

$$\Delta H_{vap}^Z = \frac{\gamma}{\gamma-1} \frac{T\alpha}{P\beta_T} P (\nu - \nu_l) = \frac{\gamma}{\gamma-1} \frac{T}{P} \left(\frac{\partial P}{\partial T} \right)_V P (\nu - \nu_l) < \Delta H_{vap}$$

$$h^Z = \frac{\Delta H_{vap}^Z}{\Delta H_{vap}} = \frac{\gamma}{\gamma-1} \frac{\alpha}{\beta_T} \frac{T(\nu - \nu_l)}{\Delta H_{vap}} = \frac{\gamma}{\gamma-1} \frac{\alpha}{\beta_T} \frac{dT}{dP} < 1$$

$$h^Z = \frac{\Delta H_{vap}^Z}{\Delta H_{vap}} = \frac{\gamma}{\gamma-1} \left(\frac{\partial P}{\partial T} \right)_V \frac{T(\nu - \nu_l)}{\Delta H_{vap}} = \frac{\gamma}{\gamma-1} \left(\frac{\partial P}{\partial T} \right)_V \frac{dT}{dP} < 1$$

To conclude this paper, we calculate the latent heat index h^Z for the following gas:

$$h_{H_2O}^Z \cong 1/2 \ 257 \ 480 \times 1.69468 \times 100 \ 000 \times 1.3368/0.3368 = 0.297965$$

$$h_{H_2O}^Z \cong 0.000279657 \times 100 \ 000 / 372.742 \times 1.3368/0.3368 = 0.297794$$

$$h_{CO_2}^Z \cong 1/2 \ 256540 \times 1.69402 \times 518 \ 000 \times 1.324/0.324 \times 1.05320 = 0.365926$$

$$h_{N_2O_4}^Z \cong 1/415 \ 000 / 2.853 \times 100 \ 000 \times 1.262/0.262 = 0.406826$$

$$h_{C_2H_6O}^Z \cong 1/855 \ 000 / 1.627 \times 100 \ 000 \times 1.14/0.14 = 0.603018$$

$$h_{He}^Z \cong 1/20 \ 500 / 16.9 \times 100 \ 000 \times 1.66/0.66 = 0.725978$$

, at $P = 100 \text{ kPa}$ with the approximations: $\nu - \nu_l \cong \nu$ and $T\alpha \cong P\beta_T \cong 1$. In the CO_2 case, the pressure P is the triple pressure and $T\alpha/(P\beta_T) \cong 1.0532$ with the Van der Waals gas approximation.

We calculate also the latent heat index h^Z for H_2O at the triple point with both formulas:

$$h_{H_2O}^Z \cong 1/2 \ 500 \ 919 \times 206.1846 \times 611.657 \times 1.32854/0.32854 = 0.20384$$

$$h_{H_2O}^Z \cong 0.0224989 \times 611.657 / 273.16 \times 1.32854/0.32854 = 0.20403$$

, at $P = 611.657 \text{ Pa}$ with the approximations: $\nu - \nu_l \cong \nu$ and $T\alpha \cong P\beta_T \cong 1$.

As the temperature T approaches the critical temperature T_{cr} , the isothermal compressibility is arbitrary large. Intuitively, from the heat engine operation in the

neighborhood of the critical point, we deduce $\bar{\delta}P \rightarrow 0$ which implies $h^Z \rightarrow 0$. As the temperature T approaches the critical temperature T_{cr} , the heat capacity ratio γ is arbitrary large. Therefore, $\gamma/(\gamma - 1)$ approaches 1 and from the expression of h^Z we deduce the thermodynamic variable $\alpha/\beta_T = (\partial P/\partial T)|_V$ approaches 0. Finally, as the temperature T approaches the critical temperature T_{cr} , the Van der Waals gas thermodynamic variable $\alpha/\beta_T = (\partial P/\partial T)|_V$ approaches $4 P_{cr}/T_{cr}$ and the Redlich–Kwong gas thermodynamic variable $\alpha/\beta_T = (\partial P/\partial T)|_V$ approaches $5.58043 P_{cr}/T_{cr}$ which implies the Van der Waals gas and the Redlich–Kwong gas can not be a real gas in the neighborhood of the critical point.

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