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Latent Work and Latent Heat of the Liquid/Vapor Transformation

by Michael A. Grinfeld and Steven B. Segletes

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14. ABSTRACT

The key elements of the theory of the liquid/vapor phase transformations are the phase equilibrium curve pressure/temperature and latent heat of the transformation. To the best of our knowledge, nobody has yet analyzed the latent *work* of phase transformation. In this report, we try to eliminate this paradoxical gap. Through a generalized methodology, we study the latent heat and latent work of liquid/vapor phase transformation for variously constrained thermodynamic processes.

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1. Introduction

The theory of phase equilibrium for the "liquid/vapor" phase transformation has been under development for centuries. In the case of one-component phases, it is presented in a very clear form in multiple classical monographs and textbooks.[1–3] The key products of the classical theory of liquid/vapor phase co-existence are chemical potentials μ of the phases and the phase equilibrium curve $p = p(T)$. The phase equilibrium curve gives the pressure p at equilibrium as a function of the absolute temperature T. This curve is universal in the sense that it does not depend upon the mechanical and thermal loading conditions. In other words, it is one and the same for isothermal and adiabatic systems as well as for isochoric or isobaric loading conditions. In short, the equilibrium pressure p depends upon the absolute temperature T alone. In the work that follows, we consider the liquid and vapor phases as co-existing without co-mingling. That is, the two phases are in contact and may transport mass and heat across a notional divide that separates them.

Consider a substance with the specific internal energy density $e = e(\rho, \eta)$, where ρ is the mass density and η is the specific entropy density. In order to find the function $p(T)$, one has to use the following three equilibrium conditions:

$$p_1 = p_2, \quad T_1 = T_2, \quad \mu_1 = \mu_2 \quad , \tag{1}$$

where 1 and 2 refer to the liquid and vapor phases, respectively.

The first of the relationships in Eq. 1 reflects the mechanical equilibrium between phases, the second reflects the thermal equilibrium between the phases, and the third reflects the "chemical" equilibrium. In this context, the chemical equilibrium means the equilibrium with respect to mass exchange between the phase in the process of vaporization/condensation.

Thermodynamical identities allow one to express p, T, and μ in terms of the derivatives of the internal energy density function $e(\rho, \eta)$:

$$p(\rho, \eta) \equiv \rho^2 \frac{\partial e(\rho, \eta)}{\partial \rho} = \rho^2 e_\rho \quad T(\rho, \eta) \equiv \frac{\partial e(\rho, \eta)}{\partial \eta} = e_\eta$$
$$\mu \equiv e + \frac{p}{\rho} + T\eta = e + \rho e_\rho + \eta e_\eta \tag{2}$$

Analysis of the system 1, which can be found in any thermodynamics textbook, results in the

following equation, known as the Clausius-Clapeyron equation:[1, 2]

$$\frac{dp(T)}{dT} = \frac{\eta_1 - \eta_2}{\rho_1^{-1} - \rho_2^{-1}} = \frac{L}{T\left(\rho_1^{-1} - \rho_2^{-1}\right)} \quad . \tag{3}$$

The quantity $L \equiv T\left(\eta_1 - \eta_2\right)$ is called the latent heat of phase transformation and appears to be a *state* function, not a *process-dependent* function. In other words, the latent heat L depends only on the thermodynamic state, regardless of whether this state was achieved by way of isochoric, isothermal, or any other particular process.

To make our point regarding L more clear, let us compare it with the similar concept of the specific heat C. Consider any process, in which the heat supply Q and the absolute temperature T are functions of time $t: Q = Q(t)$, $T = T(t)$. Then, the heat capacity C of this process is a function of time also $C = C(t)$. Here, the heat capacity $C(t)$ in the process is defined as

$$C(t) \equiv \frac{dQ(t)/dt}{dT(t)/dt} \quad . \tag{4}$$

Obviously, the function $C(t)$ essentially depends on the process under consideration. During an adiabatic process it is equal to zero, whereas for an isothermal process it is equal to infinity, etc. Using the First and Second Laws of Thermodynamics, we get, in addition to Eq. 4, the following formula for the heat capacity in an isochoric process, in terms of the specific free energy function $\psi(\rho, T) = e - \eta T$:

$$C_v = T\frac{\partial^2 \psi(\rho, T)}{\partial T^2} \equiv T\,\psi_{TT} \quad . \tag{5}$$

Although, originally, the function C_v was introduced by formula 4 applied to the isochoric process, in fact, according to formula 5, it is a function of thermodynamic state (ρ, T) only. In other words, it can be introduced directly with formula 5 and without mentioning of any particular thermodynamic process.

In addition to C_v one can introduce the specific heat C_p for the isobaric or any other specified thermodynamic process. That would lead us to other analogies of Eq. 5 and additional state functions.

If we introduce the state function C_v directly with the help of identity 5, we cannot help asking the question, "In what thermodynamic process will the function $T\,\psi_{TT}$ be equal to the heat capacity of the process?" In our case, the answer is almost a trivial tautology: "The function $T\,\psi_{TT}$ gives the heat capacity in the isochoric process." But it is not always so obvious. For instance, the quantity $L \equiv T\left(\eta_1 - \eta_2\right)$ is obviously a state function—it is defined only in terms of

state variables, without any mention of the particular process of phase transformation. However, the very name "the latent heat of phase transformation" says to us that it is the rate of heat supply in a certain thermodynamic process. Unfortunately, the classical textbooks rarely specify clearly the process for which $L \equiv T\left(\eta_1 - \eta_2\right)$ is the rate of heat supply. The lacking analysis creates the impression that $L \equiv T\left(\eta_1 - \eta_2\right)$ describes the latent heat for any thermodynamic process. This is what practitioners tacitly assume and they are surprised when somebody claims that this is a stretched interpretation. That is why, in this report, we come back to the discussion of the latent heat concept. We deliberately limit ourselves to the simplest classical one-component system "liquid/vapor," which everyone has learned in high school and college.

We believe that the general situation will become much more transparent if we introduce the concept of "the latent heat capacity $L(t)$ in thermodynamic process" similar to the concept of "the specific heat capacity in thermodynamic process." Contrary to the latent heat $L \equiv T\left(\eta_1 - \eta_2\right)$, the latent heat $L(t)$ is not a state function. However, for more narrow classes of thermodynamic processes, it leads to novel state functions. In addition, we introduce a novel thermodynamic concept of "the latent work in thermodynamic process," which is as meaningful as the concept of "the latent heat capacity in thermodynamic process."

2. Latent Heat and Work of Thermodynamic Process

Consider a single-component, two-phase heterogeneous system "liquid/vapor" (see Fig. 1) in a pressurized vessel. If the piston position is fixed, then the phase transformation occurs in the isochoric regime. Also, we assume the system can be thermally isolated (adiabatic phase transformation) or placed within a thermostat (isothermic regime.) In what follows, we mark as 1 and 2 the parameters of the liquid and vapor phases, respectively.

Consider any process "x" in the two-phase heterogeneous system under study. Then, depending on the pressure and thermal loading, the external heat supply Q, pressure P, and total volume V_{tot} become functions of time. The same is true regarding the thermodynamic parameters of the phases ρ_1, p_1, η_1, e_1, ψ_1, etc., and ρ_2, p_2, η_2, e_2, ψ_2, etc. Generally speaking, thermodynamic processes are accompanied by the evolution of the total mass components M_1, M_2.

The total mass of the substance M_{tot} is assumed fixed,

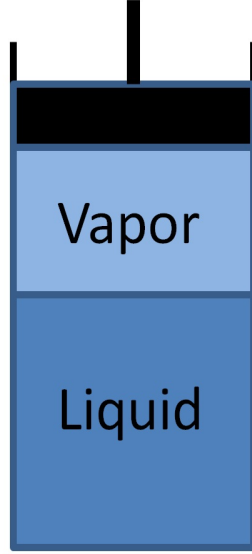$$M_1\left(t\right) + M_2\left(t\right) = M_{\text{tot}} \quad , \tag{6}$$

Fig. 1 Heterogeneous system
liquid/vapor under pressure

or in differential form

$$\frac{dM_1(t)}{dt} + \frac{dM_2(t)}{dt} = 0 \quad . \tag{7}$$

We define the latent heat of condensation $L_x(t)$ in the process "x" by the ratio

$$L_x(t) \equiv \frac{dQ(t)/dt}{dM_1(t)/dt} \quad . \tag{8}$$

Likewise, we define the latent work of condensation $W_x(t)$ in the process "x" by the ratio

$$W_x(t) \equiv P(t)\frac{dV_{\mathrm{tot}}(t)/dt}{dM_1(t)/dt} \quad . \tag{9}$$

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3.   Equations of Phase Equilibrium

Regardless of the external mechanical and thermal loading, the following phase equilibrium conditions should be satisfied:

i) the condition of mechanical equilibrium,

$$p_1 = p_2 \quad \text{or} \quad \left(\rho^2 e_\rho\right)_1 = \left(\rho^2 e_\rho\right)_2 \quad ; \tag{10}$$

ii) the condition of thermal equilibrium,

$$T_1 = T_2 \quad \text{or} \quad e_{\eta 1} = e_{\eta 2} \quad ; \text{ and} \tag{11}$$

iii) the condition of equilibrium with respect to mass exchange between phases,

$$\chi_1 = \chi_2 \quad \text{or} \quad (e + \rho e_\rho - \eta e_\eta)_1 = (e + \rho e_\rho - \eta e_\eta)_2 \quad , \tag{12}$$

which is alternately expressible as

$$(\psi + p/\rho)_1 = (\psi + p/\rho)_2 \quad . \tag{13}$$

The quantity χ is known as the chemical potential of the one-component liquid (or gaseous) phase. Therefore, condition 12 can be called the chemical equilibrium condition, although no chemical reactions are actually occur in the transformation under consideration.

Also, the mass conservation condition should be satisfied for any external loading. All additional conditions depend on the specifics of the external loading associated with process x.

4.   Vaporization/Condensation under Fixed Pressure and Prescribed Heat Supply

When external pressure is fixed $p = p_0$ the vaporization/condensation process can be controlled by the external heat supply $Q(t)$.

Differentiating the phase equilibrium Eqs. 10–12 along the process trajectory allows us to obtain

governing relationships. First, Eq. 10:

$$\left(\rho^2 e_{\rho\eta} \frac{d\eta}{dt} + \rho \left(\rho e \right)_{\rho\rho} \frac{d\rho}{dt} \right)_1 = \left(\rho^2 e_{\rho\eta} \frac{d\eta}{dt} + \rho \left(\rho e \right)_{\rho\rho} \frac{d\rho}{dt} \right)_2 = \frac{dp_{\text{ext}}}{dt} \equiv 0 \quad , \tag{14}$$

where p_{ext} is the constant external applied pressure. Equation 14 implies

$$\frac{d\rho_1}{dt} = - \left(\frac{\rho e_{\rho\eta}}{\left(\rho e \right)_{\rho\rho}} \right)_1 \frac{d\eta_1}{dt} \quad , \qquad \frac{d\rho_2}{dt} = - \left(\frac{\rho e_{\rho\eta}}{\left(\rho e \right)_{\rho\rho}} \right)_2 \frac{d\eta_2}{dt} \quad . \tag{15}$$

Then, differentiating the condition of thermal equilibrium, Eq. 11, we get

$$\left(e_{\eta\eta} \frac{d\eta}{dt} + e_{\eta\rho} \frac{d\rho}{dt} \right)_1 = \left(e_{\eta\eta} \frac{d\eta}{dt} + e_{\eta\rho} \frac{d\rho}{dt} \right)_2 \quad . \tag{16}$$

Finally, differentiating the condition of chemical equilibrium, Eq. 12, we get after some algebraic manipulations

$$\left[\left(\left(e\rho \right)_{\rho\rho} - \eta e_{\eta\rho} \right) \frac{d\rho}{dt} + \left(e_{\eta\rho}\rho - \eta e_{\eta\eta} \right) \frac{d\eta}{dt} \right]_1$$
$$= \left[\left(\left(e\rho \right)_{\rho\rho} - \eta e_{\eta\rho} \right) \frac{d\rho}{dt} + \left(e_{\eta\rho}\rho - \eta e_{\eta\eta} \right) \frac{d\eta}{dt} \right]_2 \tag{17}$$

The system given by Eqs. 15–17 can be rewritten in the following matrix form:

$$\left[\mathbf{G}_p \right] \begin{bmatrix} d\rho_1/dt \\ d\eta_1/dt \\ d\rho_2/dt \\ d\eta_2/dt \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad , \tag{18}$$

where $\mathbf{G}_p$ is the following 4×4 matrix:

$$\left[\mathbf{G}_p \right] \equiv \begin{bmatrix} \left(\rho \left(\rho e \right)_{\rho\rho} \right)_1 & \left(\rho^2 e_{\rho\eta} \right)_1 & 0 & 0 \\ 0 & 0 & \left(\rho \left(\rho e \right)_{\rho\rho} \right)_2 & \left(\rho^2 e_{\rho\eta} \right)_2 \\ e_{\eta\rho 1} & e_{\eta\eta 1} & -e_{\eta\rho 2} & -e_{\eta\eta 2} \\ \left(\left(e\rho \right)_{\rho\rho} - \eta e_{\eta\rho} \right)_1 & \left(e_{\eta\rho}\rho - \eta e_{\eta\eta} \right)_1 & - \left(\left(e\rho \right)_{\rho\rho} - \eta e_{\eta\rho} \right)_2 & - \left(e_{\eta\rho}\rho - \eta e_{\eta\eta} \right)_2 \end{bmatrix} . \tag{19}$$

The determinant of the matrix $\mathbf{G}_p$ is given by the following formula:

$$|\mathbf{G}_p| \equiv \begin{vmatrix} \left(\rho\,(\rho e)_{\rho\rho}\right)_1 & (\rho^2 e_{\rho\eta})_1 & 0 & 0 \\ 0 & 0 & \left(\rho\,(\rho e)_{\rho\rho}\right)_2 & (\rho^2 e_{\rho\eta})_2 \\ e_{\eta\rho 1} & e_{\eta\eta 1} & -e_{\eta\rho 2} & -e_{\eta\eta 2} \\ 0 & 0 & (\eta e_{\eta\rho})_2 - \eta_1 e_{\eta\rho 2} & (\eta e_{\eta\eta})_2 - \eta_1 e_{\eta\eta 2} \end{vmatrix}$$

$$= (\eta_1 - \eta_2)\left(\rho\,(\rho e)_{\rho\rho}\,e_{\eta\eta} - (\rho e_{\rho\eta})^2\right)_1 \left(\rho\,(\rho e)_{\rho\rho}\,e_{\eta\eta} - (\rho e_{\rho\eta})^2\right)_2 \quad . \tag{20}$$

Introducing the specific volume v, instead of ρ, as $v = 1/\rho$, we can rewrite Eq. 20 as

$$|\mathbf{G}_p| \equiv (\eta_1 - \eta_2)\,v_1^2\left(e_{vv}e_{\eta\eta} - e_{v\eta}^2\right)_1 v_2^2\left(e_{vv}e_{\eta\eta} - e_{v\eta}^2\right)_2 \quad . \tag{21}$$

According to the classical thermodynamic inequality, we have

$$e_{vv}e_{\eta\eta} - e_{v\eta}^2 > 0 \quad . \tag{22}$$

Since $\eta_1 - \eta_2 \neq 0$, we conclude that

$$|\mathbf{G}_p| \neq 0 \quad .$$

Finally, since $|\mathbf{G}_p| \neq 0$, system 18 implies

$$\frac{d\rho_1}{dt} = \frac{d\eta_1}{dt} = \frac{d\rho_2}{dt} = \frac{d\eta_2}{dt} = 0 \quad . \tag{23}$$

According to Eq. 23, because two independent thermodynamic parameters, (ρ_1, η_1) and (ρ_2, η_2), within *each* of the phases remain unchanged in the processes with fixed external pressures, all other thermodynamic parameters, including the absolute temperature, remain unchanged as well. This fact is well known in classical thermodynamics.

Let us now calculate the latent heat L_p for the isobaric vaporization/condensation. The total internal energy E and the total volume V of the system can be presented as follows:

$$E = M_1\,e(\rho_1, \eta_1) + M_2\,e(\rho_1, \eta_1) \equiv \sum_{I=1,2} M_I\,e(\rho_I, \eta_I) \quad , \tag{24}$$

$$V_{\text{tot}}(t) = V_1(t) + V_2(t) = \frac{M_1(t)}{\rho_1} + \frac{M_2(t)}{\rho_2} = \sum_I \frac{M_I}{\rho_I} \quad . \tag{25}$$

Note that, in light of Eq. 6, Eq. 25 may be alternately expressed for this two-phase,

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single-component system as

$$V_{\text{tot}}(t) = M_1(t) \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) + \frac{M_{\text{tot}}}{\rho_2} \quad . \tag{26}$$

Since all the thermodynamic parameters of the phase remain unchanged over time, we can employ the First Law of Thermodynamics to obtain the heat-transfer rate for this process as follows:

$$\frac{dQ}{dt} = \left[e_1 - e_2 + p_0 \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) \right] \frac{dM_1}{dt} \quad , \tag{27}$$

as it is implied by the following chain:

$$\begin{aligned}
\frac{dQ}{dt} &= \frac{dE}{dt} + p_0 \frac{dV_{\text{tot}}}{dt} \\
&= \frac{d}{dt} \sum_I M_I e \left(\rho_I, \eta_I \right) + p_0 \frac{d}{dt} \sum_I \frac{M_I}{\rho_I} \\
&= \sum_I \frac{dM_I}{dt} e_I + p_0 \sum_I \frac{1}{\rho_I} \frac{dM_I}{dt} \\
&= (e_1 - e_2) \frac{dM_1}{dt} + p_0 \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) \frac{dM_1}{dt} \\
&= \left[e_1 - e_2 + p_0 \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) \right] \frac{dM_1}{dt} \quad ,
\end{aligned}$$

where we have relied upon relationships 6 and 24–26.

Comparing the general definition of the latent heat of thermodynamic process with relation 27 for isobaric process, we arrive at the following relationship of L_p

$$L_p = \frac{dQ}{dM_1} = e_1 - e_2 + p_0 \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) \quad . \tag{28}$$

Using the chemical condition of phase equilibrium, Eq. 12, we can rewrite in the following classical form:

$$L_p = T_0 \left(\eta_1 - \eta_2 \right) \quad . \tag{29}$$

For the latent work W_p of vaporization/condensation at fixed external pressure we get, according

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to definition 9

$$W_p(t) \equiv p_0 \frac{dV_{\text{tot}}(t)/dt}{dM_1(t)/dt} = p_0 \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) \quad , \tag{30}$$

where the time-derivative of total volume has been obtained by taking the derivative of Eq. 26. In light of Eq. 13, the formula of the latent work, Eq. 30, can be rewritten in terms of the free energy jump:

$$W_p(t) \equiv p_0 \frac{dV_{\text{tot}}(t)/dt}{dM_1(t)/dt} = \psi_2 - \psi_1 \quad . \tag{31}$$

Now, we can rewrite the classical Clausius-Clapeyron formula, Eq. 3, in the following transparent and elegant form:

$$\frac{dp(T)}{dT} = \frac{\eta_1 - \eta_2}{\rho_1^{-1} - \rho_2^{-1}} = \frac{L_p}{W_p} \cdot \frac{p_0}{T_0} \tag{32}$$

or

$$\frac{d \ln p}{d \ln T} = \frac{T_0}{p_0} \cdot \frac{\eta_1 - \eta_2}{\rho_1^{-1} - \rho_2^{-1}} = \frac{L_p}{W_p} \quad . \tag{33}$$

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5. Vaporization/Condensation at Fixed Total Volume

When heating under fixed volume, the phase transformation temperature and pressure grow. The latent work of phase transformation W_v vanishes. The formula of the latent heat changes also. Taking the time-derivative of Eq. 25, we obtain

$$\frac{dV_{\text{tot}}}{dt} = \sum_I \frac{dV_i}{dt} = \sum_I \left(\frac{1}{\rho_I} \frac{dM_I}{dt} - \frac{M_I}{\rho_I^2} \frac{d\rho_I}{dt} \right) = 0 \quad , \tag{34}$$

while the total-mass M conservation conditions implies

$$\sum_I \frac{dM_I}{dt} = 0 \quad . \tag{35}$$

For the heat supply, we get the following relationship:

$$\frac{dQ}{dt} = T \left(\eta_1 - \eta_2 \right) \frac{dM_1}{dt} + \sum_I M_I T \frac{d\eta_I}{dt} \quad , \tag{36}$$

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as it is implied by the chain

$$\frac{dQ}{dt} = \frac{dE}{dt} = \frac{d}{dt}\sum_I M_I e_I = (e_1 - e_2)\frac{dM_1}{dt} + \sum_I M_I\left(e_{\rho I}\frac{d\rho_I}{dt} + e_{\eta I}\frac{d\eta_I}{dt}\right)$$

$$= (e_1 - e_2)\frac{dM_1}{dt} + \sum_I M_I\left(p\frac{1}{\rho_I^2}\frac{d\rho_I}{dt} + T\frac{d\eta_I}{dt}\right)$$

$$= (e_1 - e_2)\frac{dM_1}{dt} + \sum_I\left(\frac{p}{\rho_I}\frac{dM_I}{dt} + M_I T\frac{d\eta_I}{dt}\right)$$

$$= \left(e_1 - e_2 + \frac{p}{\rho_1} - \frac{p}{\rho_2}\right)\frac{dM_1}{dt} + \sum_I M_I T\frac{d\eta_I}{dt}$$

$$= T(\eta_1 - \eta_2)\frac{dM_1}{dt} + \sum_I M_I T\frac{d\eta_I}{dt} \qquad .$$

The phase equilibrium conditions imply three conditions:

i) the mechanical equilibrium condition

$$\frac{dp}{dt} = \left(\left(\rho^2 e_\rho\right)_\rho\frac{d\rho}{dt} + \rho^2 e_{\rho\eta}\frac{d\eta}{dt}\right)_1 = \left(\left(\rho^2 e_\rho\right)_\rho\frac{d\rho}{dt} + \rho^2 e_{\rho\eta}\frac{d\eta}{dt}\right)_2 \quad ; \tag{37}$$

ii) the thermal equilibrium condition

$$\frac{dT}{dt} = \left(e_{\eta\rho}\frac{d\rho}{dt} + e_{\eta\eta}\frac{d\eta}{dt}\right)_1 = \left(e_{\eta\rho}\frac{d\rho}{dt} + e_{\eta\eta}\frac{d\eta}{dt}\right)_2 \quad ; \text{ and} \tag{38}$$

iii) the "chemical" equilibrium condition

$$\frac{d\chi}{dt} = \left[\left((\rho e)_{\rho\rho} - \eta e_{\eta\rho}\right)\frac{d\rho}{dt} + (\rho e_{\eta\rho} - \eta e_{\eta\eta})\frac{d\eta}{dt}\right]_1$$

$$= \left[\left((\rho e)_{\rho\rho} - \eta e_{\eta\rho}\right)\frac{d\rho}{dt} + (\rho e_{\eta\rho} - \eta e_{\eta\eta})\frac{d\eta}{dt}\right]_2 \qquad . \tag{39}$$

The heat flux relation, Eq. 36, can be rewritten as

$$(\eta_1 - \eta_2)\frac{dM_1}{dt} + \sum_I M_I\frac{d\eta_I}{dt} = \frac{1}{T}\frac{dQ}{dt} \qquad . \tag{40}$$

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The variable dM_2/dt can be eliminated between Eqs. 34 and 35 to read

$$\sum_I \frac{M_I}{\rho_I^2} \frac{d\rho_I}{dt} + \left(\frac{1}{\rho_2} - \frac{1}{\rho_1} \right) \frac{dM_1}{dt} = 0 \quad . \tag{41}$$

In matrix form, the system of equations, Eqs. 37–41, may be expressed as

$$[\mathbf{G}_V]
\begin{bmatrix}
d\rho_1/dt \\
d\eta_1/dt \\
d\rho_2/dt \\
d\eta_2/dt \\
dM_1/dt
\end{bmatrix}
=
\begin{bmatrix}
0 \\
0 \\
0 \\
(1/T) \cdot (dQ/dt) \\
0
\end{bmatrix} , \tag{42}$$

where the matrix $[\mathbf{G}_V]$ is defined as

$$[\mathbf{G}_V] \equiv
\begin{bmatrix}
\rho\,(\rho e)_{\rho\rho 1} & \rho^2 e_{\rho\eta 1} & -\rho\,(\rho e)_{\rho\rho 2} & -\rho^2 e_{\rho\eta 2} & 0 \\
e_{\eta\rho 1} & e_{\eta\eta 1} & -e_{\eta\rho 2} & -e_{\eta\eta 2} & 0 \\
\left((\rho e)_{\rho\rho} - \eta e_{\eta\rho}\right)_1 & (\rho e_{\eta\rho} - \eta e_{\eta\eta})_1 & -\left((\rho e)_{\rho\rho} - \eta e_{\eta\rho}\right)_2 & -(\rho e_{\eta\rho} - \eta e_{\eta\eta})_2 & 0 \\
0 & M_1 & 0 & M_2 & \eta_1 - \eta_2 \\
M_1/\rho_1^2 & 0 & M_2/\rho_2^2 & 0 & \frac{1}{\rho_2} - \frac{1}{\rho_1}
\end{bmatrix} . \tag{43}$$

Thus, with Cramer's Rule, we arrive at the following formula:

$$\frac{dM_1}{dt} = -\frac{|\mathbf{U}_V|}{|\mathbf{G}_V|} \cdot \frac{1}{T} \frac{dQ}{dt} \quad , \tag{44}$$

where the matrix $[\mathbf{U}_V]$ is defined as

$$[\mathbf{U}_V] \equiv
\begin{bmatrix}
\rho\,(\rho e)_{\rho\rho 1} & \rho^2 e_{\rho\eta 1} & -\rho\,(\rho e)_{\rho\rho 2} & -\rho^2 e_{\rho\eta 2} \\
e_{\eta\rho 1} & e_{\eta\eta 1} & -e_{\eta\rho 2} & -e_{\eta\eta 2} \\
\left((\rho e)_{\rho\rho} - \eta e_{\eta\rho}\right)_1 & (\rho e_{\eta\rho} - \eta e_{\eta\eta})_1 & -\left((\rho e)_{\rho\rho} - \eta e_{\eta\rho}\right)_2 & -(\rho e_{\eta\rho} - \eta e_{\eta\eta})_2 \\
M_1/\rho_1^2 & 0 & M_2/\rho_2^2 & 0
\end{bmatrix} . \tag{45}$$

Thus, we arrive at the following formula of the latent heat at fixed volume:

$$L_V = -T \frac{|\mathbf{G}_V|}{|\mathbf{U}_V|} \quad . \tag{46}$$

6. Adiabatic Vaporization/Condensation

In the case of adiabatic vaporization/condensation, the latent heat is, by definition, equal to zero. Per Eq. 36, the adiabaticity condition reads (i.e., when $dQ/dt \equiv 0$)

$$(\eta_1 - \eta_2) \frac{dM_1}{dt} + \sum_I M_I \frac{d\eta_I}{dt} = 0. \quad . \tag{47}$$

In order to alternately derive Eq. 47, we may first obtain

$$\frac{dE}{dt} = T(\eta_1 - \eta_2) \frac{dM_1}{dt} - p \frac{dV_{\text{tot}}}{dt} + T \sum_I M_I \frac{d\eta_I}{dt} \quad , \tag{48}$$

as implied by the chain

$$\frac{dE}{dt} = \frac{d}{dt} \sum_I M_I \, e(\rho_I, \eta_I) = \sum_I \left(\frac{dM_I}{dt} e(\rho_I, \eta_I) + M_I \frac{de(\rho_I, \eta_I)}{dt} \right)$$

$$= (e_1 - e_2) \frac{dM_1}{dt} + \sum_I M_I \left(e_\rho \frac{d\rho_I}{dt} + e_\eta \frac{d\eta_I}{dt} \right)$$

$$= (e_1 - e_2) \frac{dM_1}{dt} + \sum_I M_I \left(\frac{p}{\rho_I^2} \frac{d\rho_I}{dt} + T \frac{d\eta_I}{dt} \right)$$

$$= \left[e_1 - e_2 + p \left(\frac{1}{\rho_1} - \frac{1}{\rho_2} \right) \right] \frac{dM_1}{dt} - p \sum_I \frac{dV_I}{dt} + T \sum_I M_I \frac{d\eta_I}{dt}$$

$$= T(\eta_1 - \eta_2) \frac{dM_1}{dt} - p \frac{dV_{\text{tot}}}{dt} + T \sum_I M_I \frac{d\eta_I}{dt}$$

where Eq. 34 has notably been used.

Now, combining the above with the First Law of Thermodynamics, we get

$$0 = \frac{dQ}{dt} = \frac{dE}{dt} + p \frac{dV_{\text{tot}}}{dt} = T(\eta_1 - \eta_2) \frac{dM_1}{dt} + T \sum_I M_I \frac{d\eta_I}{dt}$$

which, when divided by T, yields Eq. 47.

For the latent adiabatic work, we get the formula

$$\frac{dA_\eta}{dt} = -p \sum_I \frac{M_I}{\rho_I^2} \frac{d\rho_I}{dt} - T \sum_I M_I \frac{d\eta_I}{dt} - \frac{dM_1}{dt}(e_1 - e_2) \tag{49}$$

by noting that $dA_\eta/dt = -dE/dt$, as given in the third line of the prior chain.

The phase equilibrium conditions still imply the following:

i) the mechanical equilibrium condition

$$\frac{dp}{dt} = \left(\left(\rho^2 e_\rho \right)_\rho \frac{d\rho}{dt} + \rho^2 e_{\rho\eta} \frac{d\eta}{dt} \right)_1 = \left(\left(\rho^2 e_\rho \right)_\rho \frac{d\rho}{dt} + \rho^2 e_{\rho\eta} \frac{d\eta}{dt} \right)_2 \quad ; \tag{50}$$

ii) the thermal equilibrium condition

$$\frac{dT}{dt} = \left(e_{\eta\rho} \frac{d\rho}{dt} + e_{\eta\eta} \frac{d\eta}{dt} \right)_1 = \left(e_{\eta\rho} \frac{d\rho}{dt} + e_{\eta\eta} \frac{d\eta}{dt} \right)_2 \quad ; \text{ and} \tag{51}$$

iii) the "chemical" equilibrium condition

$$\frac{d\chi}{dt} = \left[\left((\rho e)_{\rho\rho} - \eta e_{\eta\rho} \right) \frac{d\rho}{dt} + (\rho e_{\eta\rho} - \eta e_{\eta\eta}) \frac{d\eta}{dt} \right]_1$$

$$= \left[\left((\rho e)_{\rho\rho} - \eta e_{\eta\rho} \right) \frac{d\rho}{dt} + (\rho e_{\eta\rho} - \eta e_{\eta\eta}) \frac{d\eta}{dt} \right]_2 \quad . \tag{52}$$

The system of equations given by Eqs. 47 and 49–52 can be rewritten in the following matrix form:

$$[\mathbf{G}_\eta] \begin{bmatrix} d\rho_1/dt \\ d\eta_1/dt \\ d\rho_2/dt \\ d\eta_2/dt \\ dM_1/dt \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -dA_\eta/dt \end{bmatrix} \quad , \tag{53}$$

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where $[\mathbf{G}_\eta]$ is the matrix

$$[\mathbf{G}_\eta] \equiv \begin{bmatrix} \rho\,(\rho e)_{\rho\rho 1} & \rho^2 e_{\rho\eta 1} & -\rho\,(\rho e)_{\rho\rho 2} & -\rho^2 e_{\rho\eta 2} & 0 \\ e_{\eta\rho 1} & e_{\eta\eta 1} & -e_{\eta\rho 2} & -e_{\eta\eta 2} & 0 \\ \left((\rho e)_{\rho\rho} - \eta e_{\eta\rho}\right)_1 & (\rho e_{\eta\rho} - \eta e_{\eta\eta})_1 & -\left((\rho e)_{\rho\rho} - \eta e_{\eta\rho}\right)_2 & -(\rho e_{\eta\rho} - \eta e_{\eta\eta})_2 & 0 \\ 0 & M_1 & 0 & M_2 & \eta_1 - \eta_2 \\ p\,M_1/\rho_1^2 & M_1 T & p\,M_2/\rho_2^2 & M_2 T & e_1 - e_2 \end{bmatrix}. \quad (54)$$

Thus, we arrive at the following formula:

$$\frac{dM_1}{dt} = -\frac{dA_\eta}{dt}\frac{|\mathbf{U}_\eta|}{|\mathbf{G}_\eta|}, \quad (55)$$

where $\mathbf{U}_\eta$ is the matrix

$$[\mathbf{U}_\eta] \equiv \begin{bmatrix} \rho\,(\rho e)_{\rho\rho 1} & \rho^2 e_{\rho\eta 1} & -\rho\,(\rho e)_{\rho\rho 2} & -\rho^2 e_{\rho\eta 2} \\ e_{\eta\rho 1} & e_{\eta\eta 1} & -e_{\eta\rho 2} & -e_{\eta\eta 2} \\ \left((\rho e)_{\rho\rho} - \eta e_{\eta\rho}\right)_1 & (\rho e_{\eta\rho} - \eta e_{\eta\eta})_1 & -\left((\rho e)_{\rho\rho} - \eta e_{\eta\rho}\right)_2 & -(\rho e_{\eta\rho} - \eta e_{\eta\eta})_2 \\ 0 & M_1 & 0 & M_2 \end{bmatrix}. \quad (56)$$

Thus, the specific latent work W_η of vaporization/condensation for an adiabatic process is given by the formula:

$$W_\eta = -\frac{|\mathbf{G}_\eta|}{|\mathbf{U}_\eta|} \quad (57)$$

7. Conclusion

We introduce several novel notions relating to the first-order phase transformation in liquid/vapor one-component systems. In addition to the standard state function L, called the latent heat, we introduce the concept of the latent-heat-for-the-process function L_x. Contrary to the L-function, the L_x-function is not a state function but a function that changes depending on the particular process under study. The function L_x coincides with L only for the phase transformation under fixed pressure and temperature.

We introduce the concept of the latent work W of the phase transformation. Here again, we distinguish between the latent work W as the state function and the latent-work-for-the-process function W_x.

Importantly, this report lays out a generalized methodology for obtaining the latent heat and latent work for variously constrained thermodynamic processes. Our methodology, though lengthier than the textbook derivation, is technically straightforward and can be used in different circumstances.

We calculate the L_x and W_x function for variously constrained thermodynamic processes accompanied by phase transformations. For the classical vaporization process under fixed pressure and temperature, we give a new elegant form, Eq. 33, of the celebrated Clausius-Clapeyron relationship.

8. References

1. Sears FW. An Introduction to Thermodynamics: The Kinetic Theory of Gases, and Statistical Mechanics. Reading: Addison-Wesley; 1953.

2. Callen HB. Thermodynamics. New York: Wiley & Sons; 1960.

3. Holman JP. Thermodynamics. New York: McGraw-Hill; 1974.

Appendix. A Curious Relation

Curiously, Holman[3] derives the relationship for a one-component single-phase liquid as

$$\frac{\partial p}{\partial T} = \frac{\partial \eta}{\partial v} \tag{A-1}$$

which, to some extent, is reminiscent of the Clausius-Clapeyron equation. He begins with the Helmholtz free energy $\psi = e - T\eta$, from which an exact differential may be taken:

$$d\psi = de - T\,d\eta - \eta\,dT \tag{A-2}$$

The increment of internal energy de may be eliminated by way of the heat/work energy balance, $de = T\,d\eta - p\,dv$, where v is the specific volume, equal to $1/\rho$. Substitution of this, in turn, eliminates the term $T\,d\eta$, leaving the expression

$$d\psi = -p\,dv - \eta\,dT \tag{A-3}$$

The implication of this relationship is that

$$-p = \frac{\partial \psi(T,v)}{\partial v}\ , \quad -\eta = \frac{\partial \psi(T,v)}{\partial T} \tag{A-4}$$

Furthermore, one may equate the mixed partial derivatives as follows:

$$-\frac{\partial^2 \psi}{\partial T\,\partial v} = \frac{\partial p(T,v)}{\partial T} = \frac{\partial \eta(T,v)}{\partial v} \tag{A-5}$$

The similarity of Eq. A-5 to the Clausius-Clapeyron relation of Eq. 3 is obvious, upon realizing that $(\eta_1 - \eta_2)/(\rho_1^{-1} - \rho_2^{-1})$ is simply $\Delta\eta/\Delta v$.

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