

NOTES AND CORRESPONDENCE

On the Diagnosis and Conservation of Energy During Condensation

PAUL M. TAG

Naval Environmental Prediction Research Facility, Monterey, CA 93940

4 December 1979 and 23 June 1980

ABSTRACT

The diagnosis and conservation of energy during condensation is examined. It is shown that the latent enthalpy, when defined in conjunction with the individual enthalpies of water vapor and liquid water, cannot be a function of the latent heat of condensation  $L$ , but a modified value ( $L'$ ) which is ~30% larger than  $L$ . The additional energy represented in  $L'$  can be thought of as a necessary absorption by the liquid water to bring the post-condensation air-vapor-liquid system into thermal equilibrium. The difference between  $L'$  and  $L$  is a function of the difference in specific heats of water vapor and liquid water. If we assume that  $(C_w - C_{pv})$  is constant, as is required in our energy conservation derivation,  $L'$  is shown to vary by only 0.59% when computed over the range  $-50$  to  $+60^\circ\text{C}$ ; a representative value for  $L'$  is  $3.142 \times 10^6 \text{ J kg}^{-1}$ .

1. Introduction

As the result of a recent energy diagnosis study using a three-dimensional model (Tag and Rosmond, 1980), we have uncovered an interesting point concerning the computation of energy in a system which includes condensation or evaporation of water substance. This note does not reveal anything new, but examines and explains a seeming inconsistency which can lead to incorrect energy diagnoses.

In the following sections we address first the determination of total energy in a system. Second, we examine both from a quantitative and qualitative point of view the transformation of latent enthalpy

into other energy forms through condensation. And finally, we determine, and discuss the use of, an alternate constant  $L'$  which can be used in defining latent enthalpy.

2. Total energy computation

One of the goals of Tag and Rosmond was to diagnose the transformations of energy which occur inside an inviscid cloud as the result of a phase change. To achieve this goal the energy forms as derived and defined by Murray and Koenig (1975) were divided into mean and perturbation quantities and used for diagnostic purposes. Their six energy forms are as follows:

|                                |                                                    |         |
|--------------------------------|----------------------------------------------------|---------|
| Kinetic energy (KE)            | = $\bar{\rho}_D(1 + \bar{r}_v)(u^2 + v^2 + w^2)/2$ | } . (1) |
| Potential energy (PE)          | = $\rho_D(1 + r_v + r_c)gz$                        |         |
| Thermal enthalpy, air (TEA)    | = $\bar{\rho}_D C_{pd} T$                          |         |
| Thermal enthalpy, vapor (TEV)  | = $\bar{\rho}_D r_v C_{pv} T$                      |         |
| Thermal enthalpy, liquid (TEL) | = $\bar{\rho}_D r_c C_w T$                         |         |
| Latent enthalpy (LE)           | = $\bar{\rho}_D r_v L$                             |         |
| Total energy (TE)              | = KE + PE + TEA + TEV + TEL + LE <sup>1</sup>      |         |

<sup>1</sup> Note that the "thermal enthalpies" as defined by Murray and Koenig are not enthalpies in the strictest sense. A strict determination of enthalpy would be based on an integration of the specific heat with respect to temperature from 0 K to the temperature in question. Such an integration is complicated by the fact that the various specific heats do not remain constant to absolute zero. As will be seen in the following section, conservation of the "enthalpy" forms in (1) stems from a

derivation in which  $C_{pd}$ ,  $C_{pv}$  and  $C_w$  are assumed constant (this assumption is reasonable over the normal range of atmospheric temperature). Theoretically, it would not be necessary to make this assumption to arrive at an expression for TE in (1). Pragmatically, however, because such an expression would involve unknown integrations involving specific heats, the assumption of specific heat invariability is desirable.

Here  $\rho_D$  is the dry air density;  $C_{pd}$ ,  $C_{pv}$ ,  $C_w$  are the specific heats of dry air, water vapor and liquid water;  $T$  the absolute temperature; and  $r_v$ ,  $r_c$  the mixing ratios of water vapor and liquid water. Other symbols have their customary definitions. Murray and Koenig's final expression for energy conservation included two additional terms, one involving the pressure perturbation and the second involving subgrid turbulent diffusion. Both of these additional terms were considered negligible by Murray and Koenig.

In our use of (1) in Tag and Rosmond (1980),  $\rho_D$  was used in place of  $\bar{\rho}_D$  in TEA, TEV, TEL and LE; because variations in density can be of the same order as those for temperature, the change to total dry air density was found to be necessary. But, in addition, we found that the latent heat of condensation  $L$  is not the correct constant to use in defining latent enthalpy in the context of (1). This latter inconsistency is the subject of this note.

Of the energy forms in (1), KE and PE have their usual definitions. TEA, TEV and TEL represent the sensible heats available in the dry air, water vapor and liquid water, respectively. LE represents the amount of energy potentially available through condensation. If LE is not included in the total energy summation, condensation and its accompanying release of latent heat will increase the sensible heat of the system with no corresponding decrease in energy elsewhere. Since total energy must be conserved, LE must be included if condensation or evaporation is anticipated.

### 3. Energy transformation during condensation

#### a. A quantitative approach

A general form of the thermodynamic equation, as given by Holmboe *et al.* (1945), is

$$(C_{pd} + C_{pv}r_v)dT - (R_d + R_vr_v)Td \ln P = -Ldr_v - C_w r_c dT, \quad (2)$$

where  $R_d$  and  $R_v$  are the respective dry air and water vapor gas constants,  $P$  is total pressure, and the other symbols are as defined earlier. If we assume an isobaric pressure change, (2) reduces to

$$(C_{pd} + C_{pv}r_v + C_w r_c)dT = -Ldr_v. \quad (3)$$

At this point we can make use of Kirchhoff's equation which defines the rate of change of  $L$  with  $T$ , i.e.,

$$\frac{dL}{dT} = C_{pv} - C_w. \quad (4)$$

Substituting  $C_{pv}$  from (4) into (3) yields

$$\left[ C_{pd} + C_w(r_v + r_c) + \frac{dL}{dT} r_v \right] dT = -Ldr_v, \quad (5)$$

or since  $r_v + r_c = \text{constant}$ ,

$$d\{[C_{pd} + C_w(r_v + r_c)]T + Lr_v\} = 0. \quad (6)$$

If we assume that KE and PE in (1) are zero, Eq. (6) suggests that

$$TE = [C_{pd} + C_w(r_v + r_c)]T + Lr_v. \quad (7)$$

Note, at this point, the appearance in (7) of  $Lr_v$ , which is identical to the latent enthalpy as used by Murray and Koenig (when converted to "per unit volume" by multiplying by  $\bar{\rho}_D$ ). And, in fact,  $Lr_v$  is the quantity typically defined as latent enthalpy (see, e.g., Van Mieghem, 1973). However, the first term on the right-hand side of (7) is not broken into the separate component enthalpies for dry air, vapor and liquid water, as has been done by Murray and Koenig in (1); Eq. (7) relates both  $r_v$  and  $r_c$  to  $C_w$ , the specific heat of liquid water. However, Eq. (7) can be rearranged to yield a form compatible with (1), i.e.,

$$TE = (C_{pd} + C_{pv}r_v + C_w r_c)T + L'r_v, \quad (8)$$

where

$$L' = L + (C_w - C_{pv})T. \quad (9)$$

Kirchhoff's equation (4) implies that  $L$  can be written in the form

$$L = L_0 - (C_w - C_{pv})T, \quad (10)$$

where  $L_0$  is a constant. Eqs. (9) and (10) together suggest that  $L' = L_0 = \text{constant}$ .<sup>2</sup> Whether  $L'$  is a constant will be considered in a later section.

For the purpose of defining and understanding the individual enthalpy components, a breakdown into TEA, TEV and TEL as done in (1) and again in (8) is conceptually more understandable since each component's specific heat is used to define its individual enthalpy. As the above exercise reveals, however, such a breakdown is not consistent with the standard definition of latent enthalpy  $Lr_v$ . Murray and Koenig's oversight in deriving LE in (1) stemmed simply from an integration of (3) without acknowledging the variation of  $L$ ,  $r_v$  and  $r_c$ .

The following section provides a physical explanation illustrating the difference between  $L'$  and  $L$ .

#### b. A physical approach

We now examine energy transformations in the following physical situation. Consider a mass of dry

<sup>2</sup> Recalling the comment in footnote 1, it would be possible to derive (7) in two parts—one part valid above a specified  $T_0$  (e.g., 0°C) where specific heats can be assumed constant, and a second over the range 0 K to  $T_0$  in which specific heat variation is unknown. This second integration could be relegated to be an unknown constant. If this approach were followed,  $T$  in (9) would be replaced by  $T - T_0$  and the absolute value for  $L'$  would change. This approach has two disadvantages: 1) one need be concerned that  $T_0$  is the lowest temperature attained in the energy summations, and more importantly that 2)  $L'$  will vary with  $T_0$ . If we recognize that TE (in an absolute sense) is still unknown with either of these approaches, the assumption that  $T_0 = 0$  K is a logical simplification.

air ( $M_d$ ) in which a mass of noncondensed vapor ( $M_v$ ) exists (both per unit volume) in a super-saturated equilibrium state (assuming clean air) at temperature  $T$ . For simplicity in defining the energies in (1), we assume that this parcel of dry air and vapor is at rest and at  $z = 0$  (i.e., there is no KE or PE). As a result, we have only three forms of energy initially—the sensible heats of the dry air and vapor (TEA, TEV) and the latent enthalpy (LE).

We now assume that condensation occurs spontaneously (e.g., through the introduction of condensation nuclei) and that the excess (supersaturated) vapor is converted into liquid. It is the equilibrium state which exists prior to, and just after, this change of phase that is of interest here. Let us consider the relevant energy transformations in detail.

During the condensation process we know that a certain amount of heat, as defined by the latent heat of condensation  $L$ , is released. This energy warms, sensibly, the resulting parcel components:  $M_d$  the mass of dry air,  $M_c$  the newly created mass of liquid (cloud water), and  $(M_v - M_c)$  the remaining mass of water vapor. We can compute the resulting change in temperature using (8), by equating the total energy which exists prior to and after condensation:

$$TE_{\text{before}} = (C_{pd} + C_{pv}r_v)T + L'r_v, \quad (11)$$

$$TE_{\text{after}} = [C_{pd} + C_{pv}(r_v - r_c) + C_w r_c](T + \Delta T) + L'(r_v - r_c). \quad (12)$$

Equating (11) and (12) then yields

$$\Delta T = \frac{LM_c}{M_d C_{pd} + (M_v - M_c)C_{pv} + M_c C_w} = \frac{LM_c}{(M_d + M_v)\bar{C}_p}, \quad (13)$$

where  $\bar{C}_p$  is an average specific heat for the mixture and  $L$  a mean value valid between  $T$  and  $T + \Delta T$ . Eq. (13) makes conceptual sense. It merely states that the change in temperature of a parcel composed of three elements will be a function of the amount of heat released into, and the average specific heat of, the three-component system. The following description of the energy transformations which occur above provides a qualitative argument for understanding  $L'$ .

In assessing the above physical situation, we must recognize that the newly created liquid water has been generated from water vapor which had sensible energy (TEV) prior to condensation of  $M_c C_{pv} T$ . We might thus expect the new liquid water to have this energy, plus an additional amount  $M_c C_w \Delta T$  as defined by (13)—giving a total of  $M_c C_{pv} T + M_c C_w \Delta T$ . According to (1), however, and as noted above, TEL must equal  $M_c C_w (T + \Delta T)$ . The difference in energy is  $M_c (C_w - C_{pv}) T$  and must be

obtained from somewhere if 1) the liquid water is to have an enthalpy equal to  $M_c C_w (T + \Delta T)$  (otherwise the liquid water would not be in thermal equilibrium with the dry air and remaining water vapor) and 2) total energy is to be conserved. Since the source of all of the transformed energy is LE, the amount of energy required is larger than can be produced using  $L' = L$ ; it is necessary to define  $L'$  equal to  $L + (C_w - C_{pv}) T$ . Namely, Eqs. (10) and (9) state that, for a unit mass of condensate, the amount of energy released during condensation is, in fact, equal to  $L'$ ; only an amount of energy equal to  $L$ , however, is available to warm the entire air-vapor-liquid system from  $T$  to  $T + \Delta T$ . The difference in energy,  $(C_w - C_{pv}) T$ , is entirely absorbed by the liquid water in order to ensure equilibrium in the post-condensation system. In the case of evaporation, this same energy difference would be liberated.

Note that, if we erroneously assume that  $L'$  is equal to  $L$ , Eq. (9) reduces to  $C_w = C_{pv}$ , which we know is untrue. However, going back to the qualitative argument presented above, if the specific heat of the condensed liquid, in fact, were the same as the specific heat of the vapor from which it came, then no additional energy would need be extracted from LE and  $L'$  would be equal to  $L$ .

#### 4. Determining a value for $L'$

For Kirchhoff's equation to be valid and the energy relations in (1) to hold (but using  $L'$  in LE),  $L'$  as well as  $C_{pd}$ ,  $C_{pv}$  and  $C_w$  must be constant. Using (9),  $L'$  can be computed using values of  $L$ ,  $C_{pv}$  and  $C_w$  from the *Smithsonian Meteorological Tables* (List, 1958). Two approaches are taken. In the first,  $(C_w - C_{pv})$  is assumed to be constant (as noted above) and is based on values valid at 0°C. In the second approach,  $(C_w - C_{pv})$  is allowed to vary according to the tables. The resulting two variations of  $L'$  are given in Fig. 1 along with two separate plots for  $L$ . One  $L$  plot is based on Kirchhoff's equation (4) and values of  $L$ ,  $C_w$  and  $C_{pv}$  valid at 0°C; the second is taken directly from the tables. (Note the break in scale between  $L'$  and  $L$ .)

Fig. 1 illustrates that, over the range of atmospheric temperature variation,  $L'$  can be assumed to be constant if the difference  $(C_w - C_{pv})$  is likewise assumed constant. Using a difference based on 0°C, the maximum variation over the 110° range is only 0.59%. An  $L'$  of  $3.142 \times 10^6 \text{ J kg}^{-1}$  at 0°C is a representative value for use in (8). Also evident in Fig. 1 is that the linear variation of  $L$  predicted by Kirchhoff's equation (4) does a good job of reproducing the true variation of  $L$ , which reveals a slight nonlinear tendency at temperatures below 0°C (the maximum difference at -50°C is 0.63%).

The inclusion of a variable  $(C_w - C_{pv})$  in (9) pro-

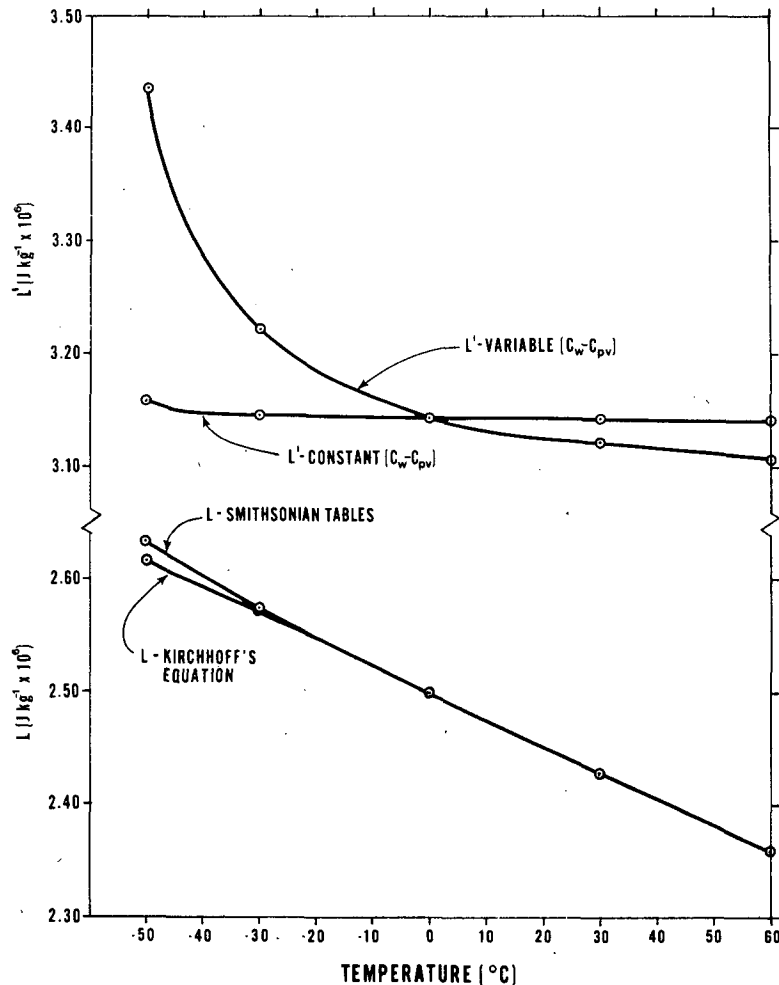


FIG. 1. Variation of  $L$  and  $L'$  with temperature. "L-Kirchhoff's Equation" uses Eq. (4) and shows the variation of  $L$  based on  $L$ ,  $C_{pv}$  and  $C_w$  defined at  $0^\circ\text{C}$ . All  $L'$  points are computed using (9); "L'-Constant ( $C_w - C_{pv}$ )" is based on  $C_w$  and  $C_{pv}$  defined at  $0^\circ\text{C}$ . Values of  $L$ ,  $C_{pv}$  and  $C_w$  are taken from the *Smithsonian Meteorological Tables* (List, 1958).

duces a much larger variation in  $L'$  —  $\sim 11\%$  difference at  $-50^\circ\text{C}$  from that at  $+60^\circ\text{C}$ . At  $0^\circ\text{C}$  the variation is  $\sim 1\%$ . These variations result from a  $(C_w - C_{pv})$  which at  $-50^\circ\text{C}$  is 60% larger than it is at  $+60^\circ\text{C}$ . The difference at  $0^\circ\text{C}$  is only 5%, however. This variation in  $L'$  at temperatures below  $0^\circ\text{C}$  is probably due to 1) inaccuracies in determining  $C_w$  and  $C_{pv}$  (below  $0^\circ\text{C}$ ,  $C_w$  is based on an extrapolation) and/or 2) the neglect of higher order terms in the thermodynamics.

### 5. Discussion and summary

The primary point of this note is that the usual definition of latent enthalpy  $Lr_v$  is not consistent with the individual contributions of liquid water enthalpy  $C_w r_c$  and water vapor enthalpy  $C_{pv} r_v$ . If it is necessary to compute total energy (e.g., for diagnostic

conservation purposes) and it is desirable to compute separate enthalpies for liquid water and water vapor [as done in Eq. (1)], a latent enthalpy based on  $L'$  in place of  $L$  is necessary.  $L'$  is approximately 30% larger than  $L$ . The difference between  $L'$  and  $L$  is  $(C_w - C_{pv})T$  and can qualitatively be thought of as the additional energy required by the liquid water (after condensation) to ensure thermal equilibrium in the post-condensation air-vapor-liquid system.

The theoretical development leading to  $L'$  requires that the specific heats  $C_w$  and  $C_{pv}$  be constant. With this assumption (using specific heats valid at  $0^\circ\text{C}$ )  $L'$  varies by only 0.59% when computed through the range  $-50$  to  $+60^\circ\text{C}$ . A representative value for  $L'$  is  $3.142 \times 10^6 \text{ J kg}^{-1}$ . If  $(C_w - C_{pv})$  is allowed to change with temperature,  $L'$  varies by  $\sim 11\%$  at  $-50^\circ\text{C}$  from its value at  $+60^\circ\text{C}$ .

This variation in  $L'$  using a variable ( $C_w - C_{pv}$ ) is probably due to inaccuracies in determining  $C_w$  and  $C_{pv}$  and/or the neglect of higher order terms in the thermodynamics.

Because our model simulations (Tag and Rosmond, 1980) do not include the freezing of liquid water, we have not addressed the latent heat of fusion  $L_f$ . If freezing of liquid water were anticipated, an additional latent enthalpy representing  $L_f$  would be necessary to ensure energy conservation in (1). And, because the specific heat of ice is different from that of liquid water (as was the case for liquid water and water vapor), a strict diagnostic conservation of energy would require an  $L_f'$  to define this new latent enthalpy [ $L_f'(r_v + r_c)$ , by analogy]. The determination of  $L_f'$  is complicated by the fact that a comparable Kirchhoff's equation for liquid/ice includes an extra term representing the change in enthalpy with pressure at constant temperature; this extra term can be considered negligible for vapor/liquid (see Iriborne and Godson, 1973, pp. 25 and 26).

To the author's knowledge the concept behind the difference in  $L$  and  $L'$  (and the resultant different definitions of latent enthalpy) has not been addressed previously in the literature. The obvious question is why. The probable reasons are that neither a detailed knowledge of the separation of TE nor an accurate determination of TE is generally needed. Murray and Koenig's intention was to examine the energetics of a cumulus cloud by assessing each individual energy component. Tag and Rosmond intended the same, but also included a careful examination of energy conservation. For most

purposes, Eq. (7) for TE could be approximated by  $C_{pd}T + Lr_v$ , in which case the traditional definition of latent enthalpy suffices and no  $L'$  need arise. However, if either an exact determination of TE or a detailed knowledge of the individual energy components is desired, the appropriate definition of LE is most important.

*Acknowledgments.* The author is indebted to Mr. Steven W. Payne of our facility for reviewing the manuscript and for his insightful discussion concerning this work. The author is grateful to Dr. Frank B. Lipps, a non-anonymous reviewer from the Geophysical Fluid Dynamics Laboratory/NOAA, for his several insightful and constructive comments. Thanks are also extended to Ms. Winona Carlisle for typing the several drafts that this manuscript has required.

#### REFERENCES

- Holmboe, J., G. E. Forsythe and W. Gustin, 1945: *Dynamic Meteorology*. Wiley, 378 pp.
- Iriborne, J. V., and W. L. Godson, 1973: *Atmospheric Thermodynamics*. *Geophys. Astrophys. Monogr.*, No. 6., Reidel, 222 pp.
- List, R. J., 1958: *Smithsonian Meteorological Tables*. Smithsonian Institution, Washington, DC, 527 pp.
- Murray, F. W., and L. R. Koenig, 1975: Cumulus cloud energetics as revealed in a numerical model of cloud dynamics: Part I. Theoretical development. *Pure Appl. Geophys.*, **113**, 909-923.
- Tag, P. M., and T. E. Rosmond, 1980: Accuracy and energy conservation in a 3-D anelastic model. To be published in *J. Atmos. Sci.*
- Van Mieghem, J., 1973: *Atmospheric Energetics*. Oxford, 306 pp.