Lecture 16 Phase Changes and Latent Heat

(Sec.4.4 of Hess)

Latent heat: When a water substance changes phase (condensation, evaporation, freezing, melting, deposition, or sublimation), a quantity of heat must be supplied to or taken away from the water substance even though the temperature remains constant.

This quantity of heat is called latent heat of phase change or simply latent heat. It has a unit of J kg⁻¹.

The following phase changes of water substance may occur in the atmosphere:



> Let L_{12} be the latent heat of change from phase 1 to 2, and L_{21} be the latent heat of change from phase 2 to 1, and apply the first law of thermodynamics to the water vapor,

$$dq = du + e_s d\alpha , \qquad (5.4.1)$$

we have

$$L_{12} = \int_{1}^{2} dq = \int_{1}^{2} (du + e_{s} d\alpha)$$

Since T and e_s are constants during the phase change, we have

$$L_{12} = (u_2 - u_1) + e_s(\alpha_2 - \alpha_1).$$

Note that the internal energy has changed, even though the temperature does not change. This is because we are talking about the change between two different phases.

 $\Delta u = 0$ for constant temperature is true only when the water substance remains in vapor phase.

Depending on what 1 and 2 are referring to, L_{12} have different names.

$$L_{melt} = (u_2 - u_1) + e_s(\alpha_2 - \alpha_1) \qquad 1 = \text{ice; } 2 = \text{water;}$$
$$e_s = \text{saturation pressure}$$
of ice-water mixture.
$$L_{evap} = (u_3 - u_2) + e'_s(\alpha_3 - \alpha_2) \qquad 2 = \text{water; } 3 = \text{vapor}$$
$$e'_s = \text{saturation vapor}$$

pressure of water and vapor.

$$L_{sub} = (u_3 - u_1) + e_s'' (\alpha_3 - \alpha_1)$$

1 = ice; 3 = vapor e_s'' = saturation vapor pressure of ice and vapor.

At the triple point, $e_s = e'_s = e''_s$, and as a result,

$$L_{sub} = L_{melt} + L_{evap}. \tag{5.4.2}$$

Change of latent heat with temperature

For evaporation (water \rightarrow water vapor),

$$L_{evap} = (u_{v} - u_{w}) + e_{s}(\alpha_{v} - \alpha_{w}).$$

Since $\alpha_w << \alpha_v$ and $e_s \alpha_v = R_v T$, we have, approximately,

$$L_{evap} = (u_v - u_w) + R_v T.$$

Thus,

$$\frac{dL_{evap}}{dT} = \frac{du_v}{dT} - \frac{du_w}{dT} + R_v.$$

Recall,

$$\frac{du_{v}}{dT} = \frac{c_{vv}dT}{dT} = c_{vv},$$

where $c_{\nu\nu}$ is the heat capacity of water vapor at constant volume and note also from the 1st law of thermodynamics, the heat capacity of water is

$$c_w = \frac{dq}{dT} = \frac{du_w}{dT} + e\frac{d\alpha_w}{dT}.$$

Again, since $d\alpha_w/dT$ is very small, we may approximate c_w by

$$c_w = \frac{du_w}{dT}.$$

Thus,

$$\frac{dL_{evap}}{dT} = c_{vv} - c_w + R_v = (c_{vv} + R_v) - c_w$$
$$= c_{pv} - c_w$$
$$= 1952 - 4218 = -2.27 \times 10^3 J \, kg^{-1} K^{-1}$$
(5.4.3)

➤ Therefore, we have shown that the rate of change of the latent heat of evaporation (condensation) with temperature (dL_{evap}/dT) is equal to $(c_{pv}-c_w)$.

Since
$$L_{evap} = 2.5 \times 10^6 J kg^{-1}$$

 $\Delta L_{evap} \approx dL_{evap}/dT \times \Delta T$
 $\Delta L_{evap} = 9.1 \times 10^4 J kg^{-1}$ at $\Delta T = 40 K$,

Since $\Delta L_{evap} \ll L_{evap}$, and we may approximately treat the latent heat of evaporation as constant.

➤ Similarly, it can be derived

$$\frac{dL_{\rm sub}}{dT} = c_{pv} - c_i.$$

Using similar arguments, we can show $L_{sublimation}$ $(L_{deposition})$ and L_{melt} $(L_{freezing})$ are also nearly constant with T:

 $L_{melt} = 0.334 \times 10^{6} J kg^{-1}, L_{sub} = 2.834 \times 10^{6} J kg^{-1}.$