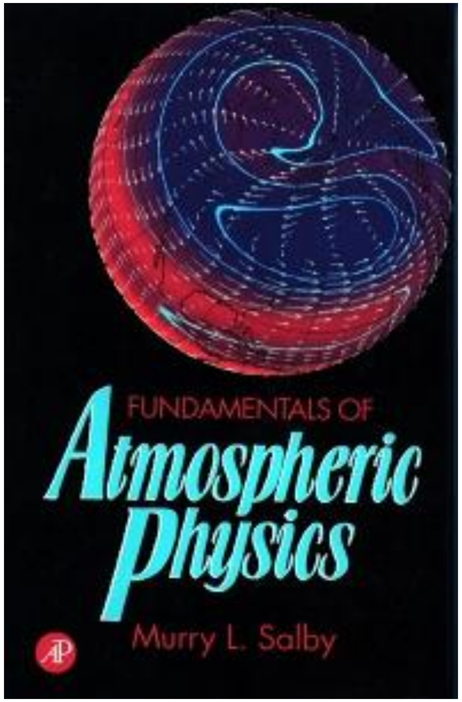
LECTURE OUTLINE

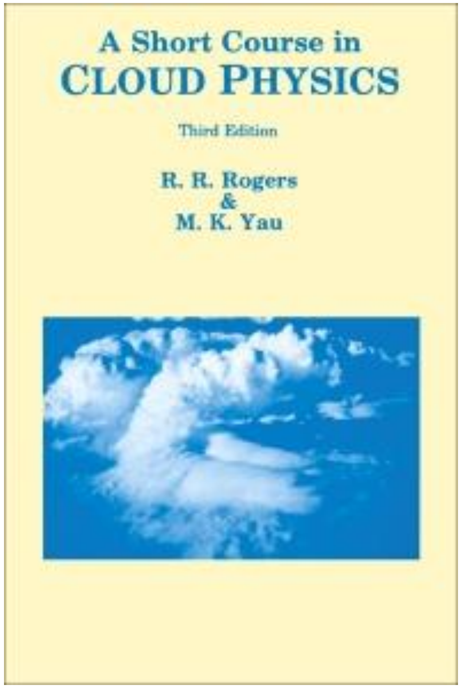
1. Equilibrium of heterogeneous system
2. Phase transformations

Salby, Chapter 4



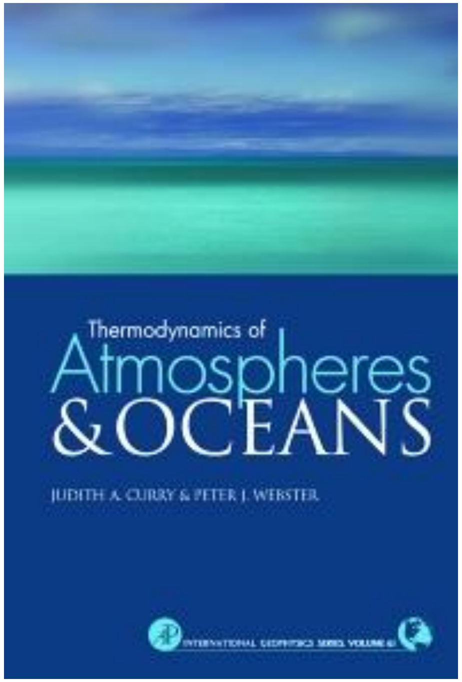
Fundamentals of Atmospheric Physics,
M.L. Salby; Salby

R&Y, Chapter 2



A Short Course in Cloud Physics,
R.R. Rogers and M.K. Yau; R&Y

C&W, Chapter 4



Thermodynamics of Atmospheres
and Oceanes,
J.A. Curry and P.J. Webster; C&W

LECTURE OUTLINE

1. Equilibrium of heterogeneous system
2. Phase transformations

Equilibrium conditions for a homogeneous system:

- thermal equilibrium
- mechanical equilibrium (at most an infinitesimal pressure difference exists between the system and its environment).

A heterogeneous system must also be in:

- chemical equilibrium.

No conversion of mass occurs from one phase to the other.

Chemical equilibrium requires a certain state variables to have no difference between the phases present.

For a homogeneous system, two intensive properties describe the thermodynamic state.

Only two state variables may be varied independently, so a homogeneous system has two thermodynamic degrees of freedom.

For a heterogeneous system, each phase may be regarded as a homogeneous sub-system, one that is ‚open’ due to exchanges with the other phases present.

The number of intensive properties that describes the thermodynamic state is proportional to the number of phases present. However, thermodynamic equilibrium between phases introduces additional constraints that actually reduce the degrees of freedom of a heterogeneous system below those of a homogeneous system.

The system we consider is a two-component mixture of:

- dry air
- water (existing in vapor and possibly one condensed phase).

Z – any extensive variable

$$Z_{tot} = Z_g + Z_c$$

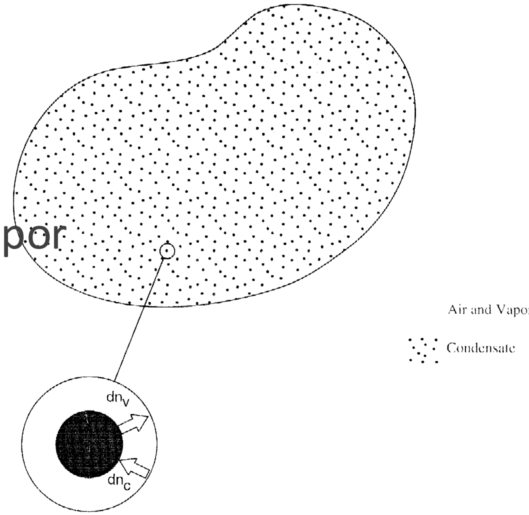
$$Z_g = Z_g(p, T, n_d, n_v)$$

$$Z_c = Z_c(p, T, n_c)$$

g – gas (air or vapor)

c – condensate

n_d, n_v, n_c– numer of mols of dry air, vapor and condensate



Changes of the extensive property Z of the individual subsystems are:

$$dZ_g = \left(\frac{\partial Z_g}{\partial T}\right)_{pn} dT + \left(\frac{\partial Z_g}{\partial p}\right)_{Tn} dp + \left(\frac{\partial Z_g}{\partial n_d}\right)_{pTn_v} dn_d + \left(\frac{\partial Z_g}{\partial n_v}\right)_{pTn_d} dn_v$$

$$dZ_c = \left(\frac{\partial Z_c}{\partial T}\right)_{pn} dT + \left(\frac{\partial Z_c}{\partial p}\right)_{Tn} dp + \left(\frac{\partial Z_c}{\partial n_c}\right)_{pT} dn_c$$

It is convenient to introduce a state variable that measures how the extensive property Z of the total system changes with an increase of one of the compenents, for example, through a conversion of mass from one phase to another.

Isobaric change of phase occurs isothermally.

The foregoing state variable is expressed most conveniently for processes that occur at constant pressure and temperature.

The partial molar property is defined as the rate at which an extensive property changes with a change in the number of mols of the kth species under isobaric and isothermal conditions.

$$\bar{z}_k = \left(\frac{\partial Z}{\partial n_k} \right)_{pTn}$$

For a system of dry air and water in which the latter appears only in trace abundance those quantities are nearly the same as molar properties.

$$\tilde{z}_k = \frac{Z}{n_k}$$

Incorporating the new notation:

$$dZ_g = \left(\frac{\partial Z_g}{\partial T}\right)_{pn} dT + \left(\frac{\partial Z_g}{\partial p}\right)_{Tn} dp + \bar{z}_d dn_d + \bar{z}_v dn_v$$

$$dZ_c = \left(\frac{\partial Z_c}{\partial T}\right)_{pn} dT + \left(\frac{\partial Z_c}{\partial p}\right)_{Tn} dp + \bar{z}_c dn_c$$

The value of the total extensive property Z is:

$$dZ_{tot} = dZ_g + dZ_c = \left(\frac{\partial Z_{tot}}{\partial T}\right)_{pn} dT + \left(\frac{\partial Z_{tot}}{\partial p}\right)_{Tn} dp + \bar{z}_d dn_d + \bar{z}_v dn_v + \bar{z}_c dn_c$$

If the system is closed, the abundance of individual components is preserved, so:

$$dn_d = 0$$

$$d(n_v + n_c) = 0$$

$$dZ_{tot} = \left(\frac{\partial Z_{tot}}{\partial T}\right)_{pn} dT + \left(\frac{\partial Z_{tot}}{\partial p}\right)_{Tn} dp + (\bar{z}_v - \bar{z}_c)dn_v$$

$$Z_{tot} = n_d\bar{z}_d + n_v\bar{z}_v + n_c\bar{z}_c$$

CHEMICAL EQUILIBRIUM

UNIVERSITY
OF WARSAW

A criterion for two phases to be at equilibrium with one another:

- in addition to thermal and mechanical equilibrium, those phases must also be in chemical equilibrium.

Chemical equilibrium is determined by the diffusion of mass from one phase to the other. This is closely related to the Gibbs function.

$$dG = -SdT + Vdp + \sum_k \left(\frac{\partial G}{\partial n_k}\right)_{pTn} dn_k$$

Gibbs function for a homogeneous system

$$G = H - TS$$

$$dG = -SdT + Vdp$$

The chemical potential for the k^th species is defined as the partial molar Gibbs function:

$$\mu_k = \bar{g}_k = \left(\frac{\partial G}{\partial n_k}\right)_{pTn}$$

It is the same as the molar Gibbs function $\tilde{g}_k$.

Specific Gibbs function is: $g_k = \frac{G_k}{m_k} = \frac{G_k}{n_k}\frac{1}{M_k} = \frac{\mu_k}{M_k}$

M_k is a molar mass

For the gas phase: $dG_g = \left(\frac{\partial G_g}{\partial T}\right)_{pn_vn_d} dT + \left(\frac{\partial G_g}{\partial p}\right)_{Tn_vn_d} dp + \mu_d dn_d + \mu_v dn_v$

In a constant n_d and n_v process (e.g. one not involving a phase transformation), this expression must reduce to the fundamental relation for a homogeneous closed system:

$$dG_g = -S_g dT + V_g dp$$

We can identify: $\left(\frac{\partial G_g}{\partial T}\right)_{pn_vn_d} = -S_g$ $\quad \left(\frac{\partial G_g}{\partial p}\right)_{Tn_vn_d} = V_g$

Since those relations involve only state variables, they must hold irrespective to path (e.g.whether or not a phase transformation is involved). Thus:

$$dG_g = -S_g dT + V_g dp + \mu_d dn_d + \mu_v dn_v$$

A similar analysis leads to relations:

for the gas phase: $dG_g = -S_g dT + V_g dp + \mu_d dn_d + \mu_v dn_v$

for the condensed phase: $dG_c = -S_c dT + V_c dp + \mu_c dn_c$

for the whole system: $G_{tot} = n_d \tilde{g}_d + n_v \tilde{g}_v + n_c \tilde{g}_c$

$$dG_{tot} = -S_{tot} dT + V_{tot} dp + (\mu_v - \mu_c) dn_v$$

$$dn_d = 0$$
$$d(n_v + n_c) = 0$$

For the heterogeneous system to be in thermodynamic equilibrium, the pressures and temperatures of the different phases present must be equal.

There can be no conversion of mass from one phase to another.

The fundamental relation for a system in equilibrium:

$$dG_{tot} \geq -S_{tot} dT + V_{tot} dp + (\mu_v - \mu_c) dn_v$$

$$p = const, T = const \implies dG_{tot} \geq (\mu_v - \mu_c) dn_v$$

for a transformation of phase that occurs at constant pressure and temperature the above expression must apply irrespective of the sign of dn_v. Therefore $\mu_v = \mu_c$.

Gibbs-Duhem equation

In thermodynamics, the Gibbs–Duhem equation describes the relationship between changes in chemical potential for components in a thermodynamic system.

$$U = TS - pV + \sum_{i=1}^{C} \mu_i n_i$$

C– number of components

A derivatives: $$dU = TdS + SdT - pdV - Vdp + \sum_{i=1}^{C} \mu_i dn_i + \sum_{i=1}^{C} n_i d\mu_i \quad (1)$$

First Law of Thermodynamics: $$dU = TdS - pdV + \sum_{i=1}^{C} \mu_i dn_i \quad (2)$$

---

(1)-(2) $$0 = SdT - Vdp + \sum_{i=1}^{C} n_i d\mu_i$$

$$\sum_{i=1}^{C} n_i d\mu_i = -SdT + Vdp$$

In a system with specified intensive parameters p and T only C-1 components of a system consisting of C components can have independent values of chemical potential.

Thermodynamic degrees of freedom
Gibbs Rule

The number of degrees of freedom (F) equals the total number of intensive variables required to specify the complete system minus the number of these variables that can be independently varied

C – the number of components; P – the number of phases

- C-1 : the number of intensive variables that define each phase
- 2 : pressure and temperature
- for P coexisting phases, the total number of of intensive variables defining the system is (C-1)P
- C(P-1) : the number of variables that cannot be independently varied; the chemical potential of each component must be equal for all phases.

$$F=(C-1)P+2-C(P-1)$$

$$F=C-P+2$$

This rule enables us to determine the number of intensive variables which may be specified in determining the state, without changing the number of components and/or phases.

In the studies of atmosphere we consider the following systems:

- moist air (dry air + water vapor): C=2; P=1
- liquid cloud (dry air + water vapor + liquid water drops): C=2; P=2
- mixed phase clouds (dry air + water vapor + liquid water drops + ice particles): C=2; P=3

If we apply the Gibbs rule to water: a one -component system (C=1), we have

F=3-P

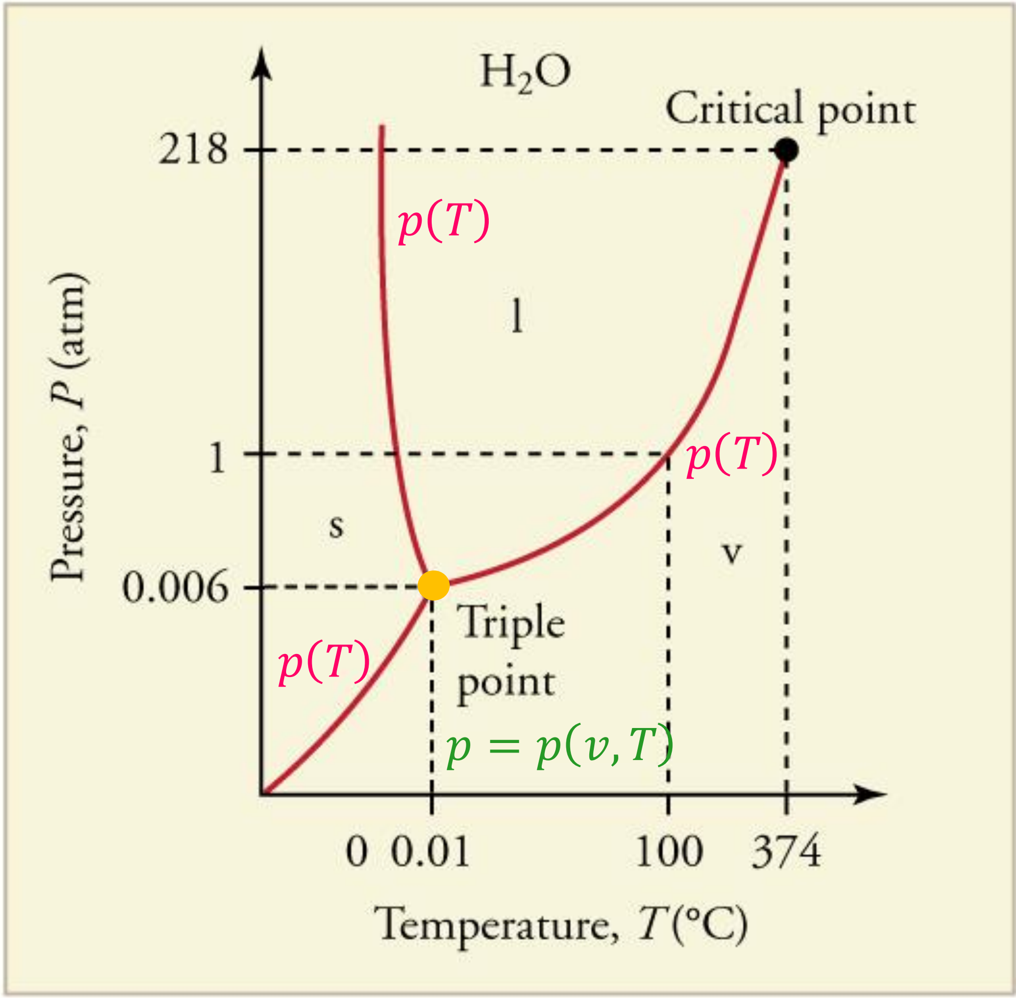
- P=1 (only water vapor), F=2

  Two variables completely specify the state: e.g. pressure and temperature. The equation of state is the ideal gas law $p = p(v,T)$
- P=2 (two phases), F=1

  One free state variable: e.g. liquid and vapor in equilibrium,

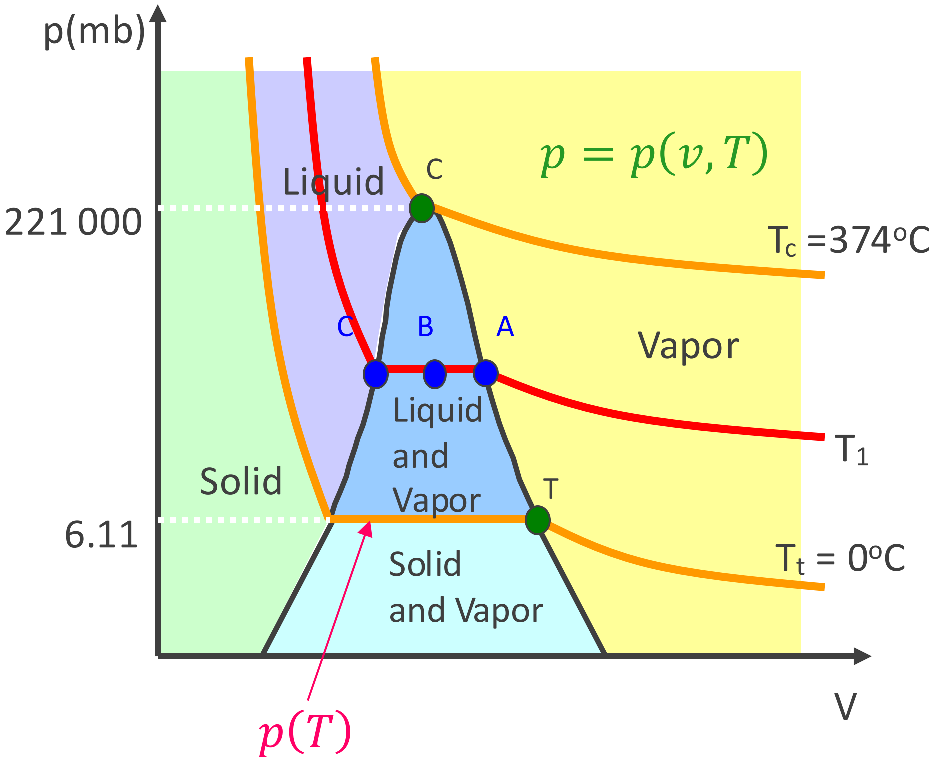
  the state is specified only by T; the equation of state takes a form $p(T)$
- P=3 (three phases), F=0

  Occurs at only one point (p,T), called the triple point.



$T_c = 647$ K, $p_c = 218.8$ atm (1atm = 1013.25 hPa)

$T_T = 273$ K, $p_T = 6.1$ hPa


p(mb)
221 000
6.11
Liquid
Solid
C
C
B
A
Vapor
Liquid and Vapor
T
Solid and Vapor
$p = p(v, T)$
T_c =374°C
T_1
T_t = 0°C
V
$p(T)$

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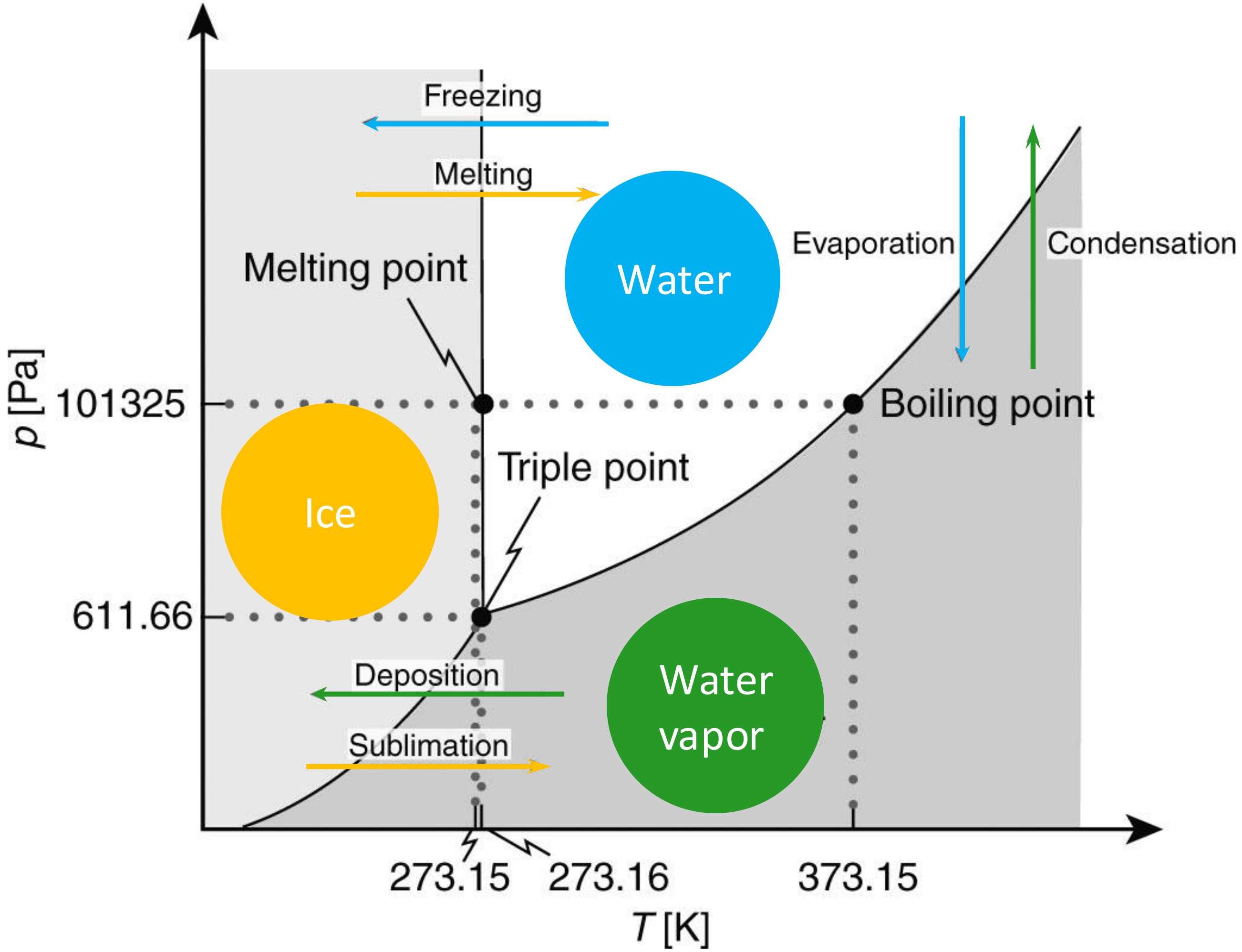


Fig.2.10 Lohmann, Luond, and Mahrt: An Introduction to Clouds. @Cambridge University Press 2016

Heat transferred during an isobaric process between two homogeneous states of the same phase is proportional to the change of temperature.

$$\delta q = c_p dT$$

Heat transfer during an isobaric process between two phases of a heterogeneous system involves no change of temperature.

The heat transfer results in a conversion of mass from one phase to the other (which is associated with a change of internal energy) and in work being performed when the system's volume changes.

The specifc latent heat of transformation is defined as the heat absorbed by the system during an isobaric phase transition (it is convenient to use the enthalpy $dh = \delta q + v dp$):

$$L = \delta q_p = dh$$

dh – the enthalpy of phase transformation

Specific latent heats of transformations:

1. liquid → vapor (vaporization): $L_{lv} = h_v - h_l$
2. solid → liquid (fusion): $L_{il} = h_l - h_i$
3. solid → vapor (sublimation): $L_{iv} = h_v - h_i$

The specific heats are related as: $L_{iv} = L_{il} + L_{lv}$

Like specific heat capacity, latent heat is a property of the system and thus it depends on the thermodynamic state, which may be expressed $L = L(T)$.

Consider two homogeneous sytems:

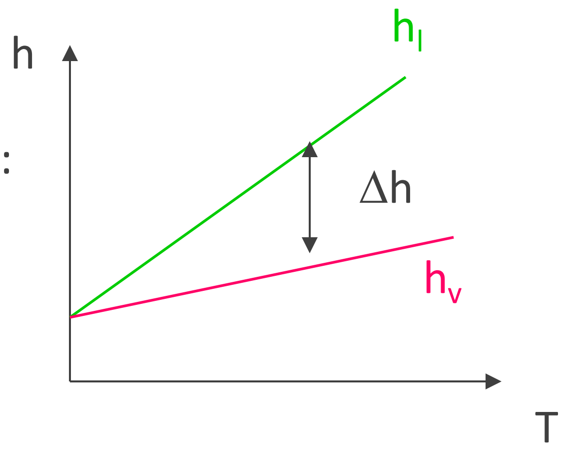
one entirely in phase 'v' and another entirely in phase 'l' (e.g. v- vapor, l – liquid).

An isobaric process between two homogeneous states that involves only one phase:

$$dh_v = \left(\frac{\partial h_v}{\partial T}\right)_p dT = c_{pv} dT \qquad dh_l = \left(\frac{\partial h_l}{\partial T}\right)_p dT = c_l dT$$

The difference of enthalpy between phases 'v' i 'l' changes with temperature.
For vaporisation we have:

$$\Delta h = h_v - h_l \quad \Longrightarrow \quad d(\Delta h) = \left(c_{pv} - c_l\right) dT$$



The enthalpy difference equals the latent heat of transformation (L):

$$L = \delta q_p = \Delta h \qquad d(\Delta h) = \underbrace{(c_{pv} - c_l)}_{\Delta c_p} dT$$

Kirchhoff's equation: $$\frac{dL}{dT} = \Delta c_p$$

Regarding the specific heats as constants, we may integrate the Kirchhoffs's equation e.g. for liquid– vapor transformation:

$$L_{lv}(T) = L_{lv0} - (c_l - c_{pv}) \cdot (T - T_0)$$

At 0ºC the latent heats of water have the values:

$$L_{vl0} = 2.50 \cdot 10^6 \text{ Jkg}^{-1}$$
$$L_{li0} = 3.34 \cdot 10^5 \text{ Jkg}^{-1}$$
$$L_{vi0} = 2.83 \cdot 10^6 \text{ Jkg}^{-1}$$

The specific heat capacities depend weakly on both temperature and pressure. c_{pv} and c_{pl} vary by only 1% over the temperature range 0ºC – 30ºC (Table on slide 28).

The latent heat (L) corresponds to a change of enthalpy during an isobaric phase transformation (p=const).

The change of specific internal energy :

$$du = \delta q - pdv \quad \longrightarrow \quad du = L - pdv$$

$$\uparrow$$

for an isobaric transformation

$$dh = \delta q - vdp$$

$$dp = 0$$

$$dh = \delta q = L$$

For fusion/melting dv is negligible:

$$dv \cong 0$$

$$du = L$$

For vaporization and sublimation the volume of vapor is much greater than the volume of liquid or ice:

$$dv \cong v_v$$

$$du = L - R_v T$$

$$pdv \cong pv_v = R_v T$$

Specific heat capacity of water

The variation of specific heat with pressure:

$$c_{pl} = \left(\frac{\partial h}{\partial T}\right)_p \quad \longrightarrow \quad c_{pl} = \frac{\partial u}{\partial T} + p\frac{\partial v}{\partial T}$$

$$h = u + pv$$

$$\frac{\partial c_{pl}}{\partial p} = \frac{\partial^2 u}{\partial T \partial p} + p\frac{\partial^2 v}{\partial T \partial p} \qquad (1)$$

$$du = Tds - pdv$$

$$\left(\frac{\partial u}{\partial p}\right)_T = T\left(\frac{\partial s}{\partial p}\right)_T - p\left(\frac{\partial v}{\partial p}\right)_T$$

Maxwell’s relation

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

$$\frac{\partial^2 u}{\partial p \partial T} = -T\frac{\partial^2 v}{\partial T^2} - p\frac{\partial^2 v}{\partial p \partial T} \qquad (2)$$

(1)+(2)

$$\frac{\partial c_{pl}}{\partial p} = -T\frac{\partial^2 v}{\partial T^2}$$

the relation may be determined easily from observations of temperature and specific volume

Specific heat capacity of water

The specific heat of pure water at surface pressure has been determined empirically to be:

$$c_{pl}(T) = 4217.4 - 3.72083 \cdot t + 0.1412855 \cdot t^2 - 2.654387 \cdot 10^{-3} t^3 + 2.093236 \cdot 10^{-5} t^4$$

$$t(℃) = T(K) - 273.15$$

$c_{pl} - c_{vl}$ for water

Since the entropy is an exact differential: $Tds = T\left(\frac{\partial s}{\partial T}\right)_v dT + T\left(\frac{\partial s}{\partial v}\right)_T dv$

Dividing by dT while holding p constant:

$$T\left(\frac{\partial s}{\partial T}\right)_p = T\left(\frac{\partial s}{\partial T}\right)_v + T\left(\frac{\partial s}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

$$c_{pl} = c_{vl} + T\left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p$$

$$c_{pl} - c_{vl} = -T\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p^2$$

$$c_p = T\left(\frac{\partial s}{\partial T}\right)_p \qquad c_v = T\left(\frac{\partial s}{\partial T}\right)_v$$

Maxwell's relation $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v$

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p$$

Because of the near incompressibility of water, there is very little difference in the values of c_{pl} and c_{vl}; it is designed by c_l.

Latent heats; specific heats

T (ºC)	L_{lv} (10^6J kg^{-1})	L_{iv} (10^6J kg^{-1})	c_i (J kg^{-1} K^{-1})	c_l (J kg^{-1} K^{-1})	c_{pv} (J kg^{-1} K^{-1})
-40	2.603	2.839	1814	4773	1856
-30	2.575	2.839	1885	4522	1858
-20	2.549	2.838	1960	4355	1861
-10	2.525	2.837	2032	4271	1865
0	**2.501**	**2.834**	**2107**	**4218**	**1870**
10	2.477			4193	1878
20	2.453			4182	1886
30	2.430			4179	1898
40	2.406			4179	1907

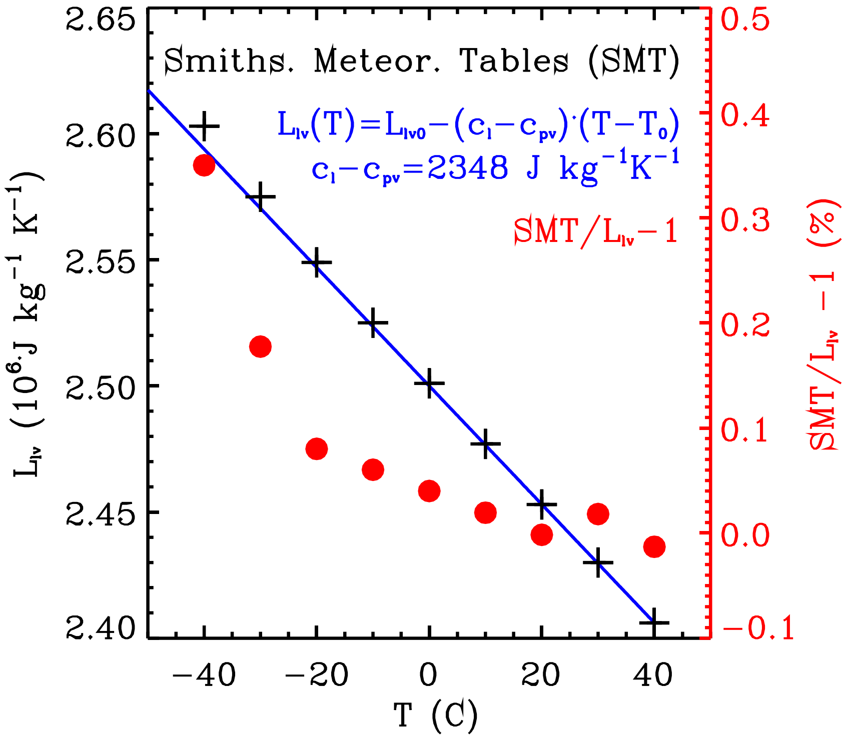
good approximation

The specific heat capacities depend weakly on both temperature and pressure. c_{pv} and c_l vary by only 1% over the temperature range 0°C – 30°C.

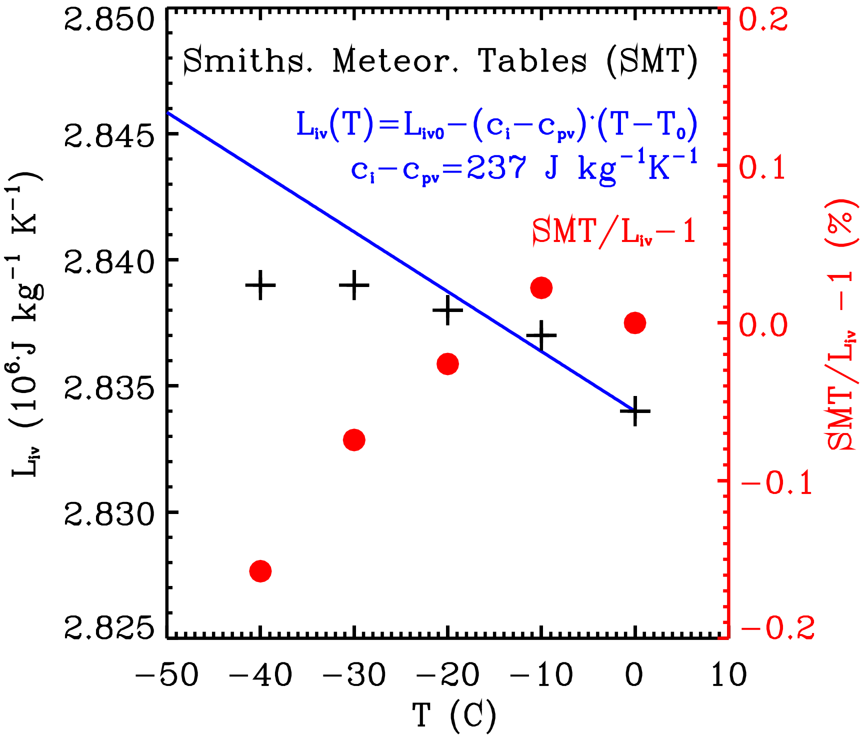
Tabele 4.2: Curry, J.A. and P.J. Webster, Thermodynamics of Atmospheres &Oceans
Smithsonian Meteorological Tables

Variation of latent heats

Latent heat of condensation L_{lv}



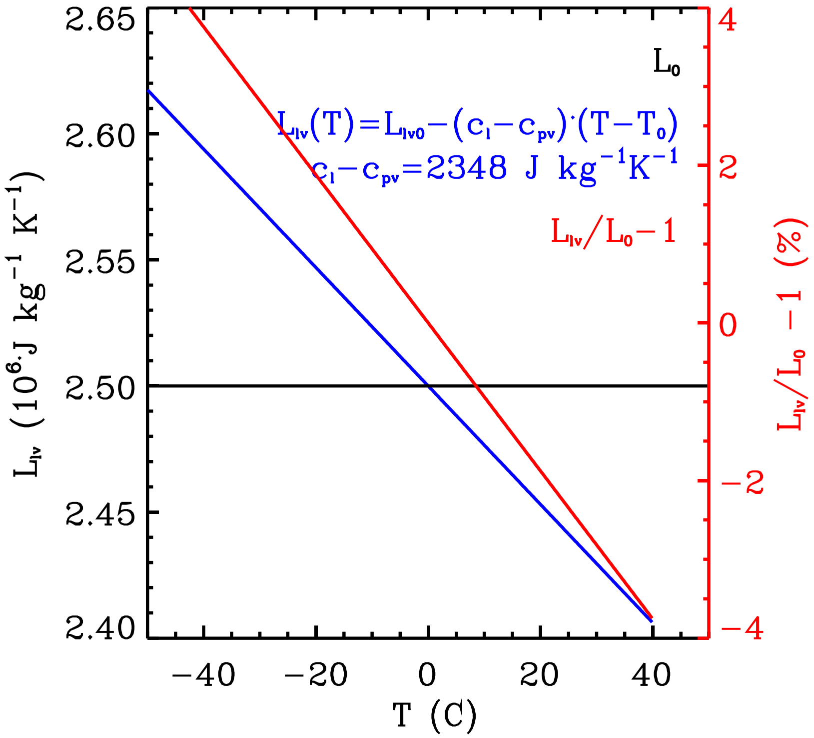
Latent heat of sublimation L_{iv}



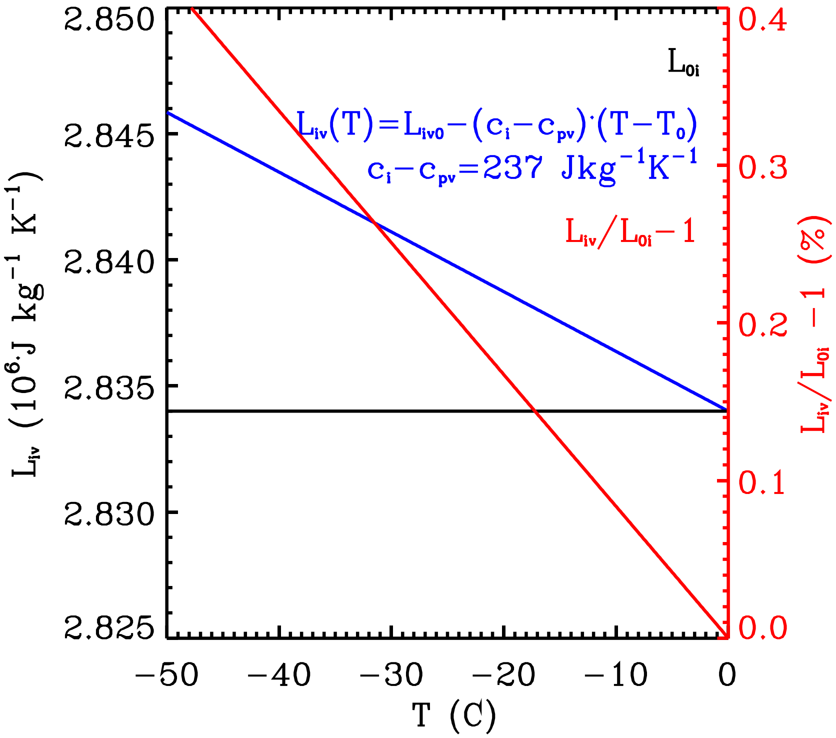
Assumption of constant values of specific heats is correct.

Is the assumption $\mathrm{L} = \mathrm{const}$ correct?

Latent heat of condensation L_{lv}



Latent heat of sublimation L_{iv}



It is INCORRECT for latent heat of condensation.

It is CORRECT for latent heat of sublimation.