Entropy, Adiabats and Potential Temperatures

A lecture held by Vilho Väisälä at a meeting of the Geophysical Society of Finland

The following paper has its basis in my earlier paper on the entropy of atmospheric air [1] to which reference may be made for the derivation of formulas and for the constants used.

For the analysis of air masses the quasi-conservative quantities are of importance. We think an air parcel separated from the surrounding air by an imagined boundary surface. Supposing

- I. that no mass exchange through the boundary of the parcel occur (a closed system) the mixing ratio of H_2O will be maintained constant;
- 2. that no heat exchange through the boundary of the parcel occur (adiabatic process) the entropy of the parcel will be maintained constant if, furthermore, the processes can be considered reversibel.

A mass exchange which implies heat exchange also occurs, e.g., in the form of rain. Supposing the rain amount as known the corresponding change in mixing ratio and in entropy can be taken into account. — In most cases the meteorological processes can be regarded very closely reversibel.

In synoptic investigations, generally, alongside the mixing ratio, different »potential temperatures» are used as conservative quantities. We are of the standpoint that the primary quantity, entropy, for certain reasons would be of interest when used instead of these »temperatures» which must be regarded as secondary quantities.

Entropy. We have made the following main suppositions:

1. dry air and water vapor are perfect gases,

- 2. the specific heat of water and ice are constant,
- 3. the entropy of a mixture is equal to the sum of partial entropies. The used notations and the base equations are as follows:

 1):

Atmospheric air

		Dry part						
		of air	Vapor	Water		Ice	Total	
Indices		а	υ		w			
Composition, Mixing ratios	Clear air	ı kg +	m_{v}			=	= 1 + m	(1a)
	Water cloud	ı » +	$m_{\mathcal{V}}$	+	m_{w}	=	= »	(1b)
	Mixed »	1 » +	$m_{\mathcal{U}}$	+	m_{w} $+$	$m_i =$	= »	(1C)
	Ice »	ı » +	m_{v}		- +	$m_i =$	= »	(1d)
P	ressures	Pa +	e			==	. P	(2)
Entropies		s_a +	$S_{\boldsymbol{v}}$	+	S_w +	$S_i =$		(3)
»		s_a +	S_{v}			==	S_g	(4)

s = specific entropy, S = some other entropy, $p_n = 1000 \text{ mb} = \text{zero}$ pressure for entropy, $T_n = 152.26^{\circ} \text{ K} = \text{zero}$ temperature for entropy, u = relative humidity, $o \leq u \leq 1$, saturation u = 1, E resp. M = partial pressure resp. mixing ratio of saturated vapor in respect of water,

(5)
$$e = uE$$
,

(6)
$$m_v = uM = \varepsilon \frac{e}{P_a}, \ \varepsilon = 0.622,$$

(7)
$$u' = u + 0.0415 \left(u \ln \frac{1}{n} \right) = \text{wirtual} \text{ humidity,}$$

$$u' - u = \Delta u \leq 0.015,$$

(8)
$$\sigma(T) = c_w \ln \frac{T}{T_n} + \frac{l}{T} = \text{specific entropy of saturated vapor,}$$

$$l = \text{heat of evaporation at } T^{\circ}K,$$

¹⁾ The notations used here are not the same as in [1].

T and u.

(9) $s_v = \sigma(T) - R_v \ln u = \text{specific entropy of water vapor,}$ $R_v = \text{gas constant of water vapor,}$

(10)
$$G(T) = \varepsilon \frac{E(T)}{p_n} \sigma(T),$$

(11)
$$S_i = m_i c_i \ln \frac{T}{T_n} =$$
 partial entropy of ice,

(12)
$$S_w = m_w c_w \ln \frac{T}{T_n} =$$
 » water,

(13)
$$S_v = m_v \ s_v = u \frac{p_n}{p_a} G(T) = \quad \text{w} \quad \text{wapor},$$

 $S_g = s_a + S_v =$ entropy of gaseous parts of air. s_a is a function of p_a and T only, m_v , S_v , S_g are functions of p_a ,

The computation of the entropies can be made graphically or by means of a special slide rule [1, p. 48].

An isentrope resp. isentropic surface is a curve resp. surface on which a named entropy (s_a, S_v, S_g, S) has a constant value. In the atmosphere they belong to a momentary (synoptic) state of air and change with time. Mostly, instead of isentropes the isolines of different potential temperatures are used in meteorological investigations. Usually the isolines of the ordinary potential temperature are in brief called isentropes and coincide with the isentropes of dry air. We use the expressions entropy and isentrope in their extended senses. Isentropes can be drawn on the aerological diagrams also [1, p. 23] These isentropes are coordinate lines as well as isobars, isotherms, adiabats etc. and have no connection with the actual weather situation.

We consider equations of the most important isentropes on an aerological diagram. They are:

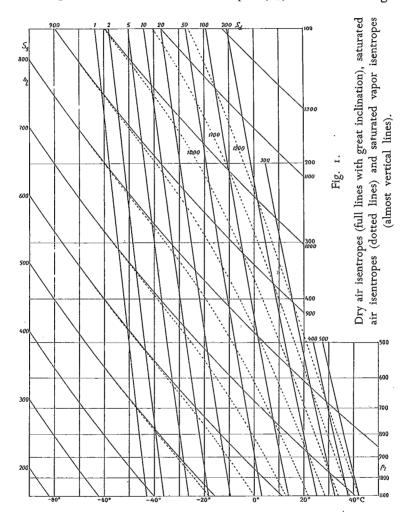
(15a) Isentrope of dry air
$$s_a(p_a, T) = \bar{s}_a^{-1}$$
)
(15b) \Rightarrow \Rightarrow saturated vapor $S_v(p_a, T, 1) = \bar{S}_v^{-2}$)
(15c) \Rightarrow \Rightarrow air $S_g(p_a, T, 1) = \bar{S}_g^{-3}$) where \bar{s}_a , \bar{S}_v , \bar{S}_g are constant.

¹⁾ This is a dry adiabat as well.

²⁾ This is almost the same as an isoline of the saturation mixing ratio M = const.

³⁾ This resembles a condensation adiabat but differs notably therefrom.

Because of (4) the curves (15c) are diagonal curves of the isentropes (15a) and (15b). Supposing $\overline{S}_g = \overline{s}_a + \overline{S}_v$ the three curves (15) intersect in the same point. A network of isentropes (15) is shown in fig. 1.1)



An universal isentrope of the total entropy can be written as (16) $S(p_a, T, m_v, m_w, m_i) = \text{const.}$ The entropy here is given by (3). To obtain a single group of curves

¹⁾ In the fig. 1 s_l , p_l and S_d respectively denote s_a , p_a and S_v .

we must have three more conditions. These usually concern the amount of H_2O in the air. The formula (16) contains all the possibilities.

An adiabat belongs to changings of the air state with time. The adiabats are drawn on aerological diagrams, so-called adiabat charts. During adiabatic reversibel changings of the state of a closed air parcel the entropy thereof remains constant. If the air parcel is not closed but looses (or gains) mass, especially water in the form of rain, the entropy brought off (resp. on) with the lost (gained) water must be taken into account as change of the entropy. When again letters with bar denote constant values we get following adiabats:

Dry adiabats:

Clear air, no condensation,
$$m_v=\overline{m}_v$$
, (17a) S_g $(p_a,\ T,\ u)=\overline{S}_g$ Dry air, $m_d={\rm o},$

$$(17b) s_a (p_a, T) = \bar{s}_a.$$

The adiabats (17a) and (17b) are practically identic.

Condensation adiabats:

Cloud adiabat:
$$S_g + S_w = \overline{S}_g$$
 (18a) $u = 1, m_v + m_w = \overline{m}_v$ No precipitation. Rain adiabat: $S_g + S_w + S_r = \overline{S}_g$ (18b) $u = 1, m_v + m_w + m_r = \overline{m}_v$
$$m_r = \int_{\overline{T}}^T dm_r = \text{rain amount along the adiabat between condensation point } (\overline{T}) \text{ and the point considered } (T).$$

$$S_r = c_w \int_{\overline{T}}^T dm_r \ln \frac{T}{T_n} = \text{entropy of rain.}$$
 Pseudo-adiabat: $S_g + S_r = \overline{S}_g$

(18c) $u=1, \ m_w=0, \ m_v+m_r=\overline{m}_v$ The entropy of rain on the pseudo-adiabat can be written also as

(19)
$$S_r = c_w \left(\overline{M} \ln \frac{\overline{T}}{T_n} - M \ln \frac{T}{\overline{T}_n} \right) - c_w \int_T^{\overline{T}} M \, d\ln T.$$

We supposed the cloud and precipitation to consist of water.

We consider now an adiabatically rising air parcel, the original (non saturated) state of which (A) possesses the entropies \bar{s}_a , \bar{S}_v , \bar{S}_g . The air parcel rises first along the dry adiabat (17a) (which can be substituted with 17b) up to the condensation point (K). At K the three entropies have the same values \bar{s}_a , \bar{S}_v , \bar{S}_g as in A. Above K the state of the air parcel changes along one of the condensation adiabats (18). If no precipitation occurs, the adiabat is (18a), the cloud adiabat. This is, in the beginning of condensation, mostly the case in reality. If all the condensed water immediately also precipitates we have the pseudo-adiabat (18c). This never happens in nature. In other cases where the condensed water precipitates in part only we have one of the rain adiabats (18b). This adiabat will be defined only when the law of precipitation is known.

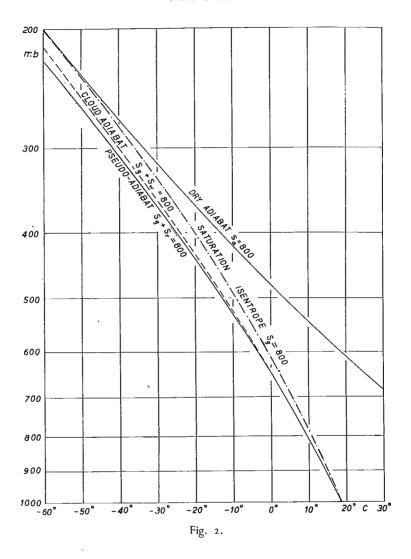
We computed in fig. 2 some isentropes and adiabats with the entropy 800 J/° C, namely

- A. the dry adiabat $s_a = 800$, which also is a dry air isentrope,
- B. the saturated air isentrope $S_q = 800$,
- C. the cloud adiabat $S_g + \bar{S}_w = 800$,
- D. the pseudo-adiabat $S_q + S_r = 800$.

The following table contains pressure coordinates of these curves (except the first one) at some temperatures:

°C	18.5	14.7	10.4	5.4	o.8	<u> </u>	— <u>1</u> 9.5	—3 <i>5</i> .5	6o.o	<u>84.5</u>
B mb C » D » D—C »	0 I 000	910.4	800 819.4 819.6 0.2	726.5 727.5	632.2 634.3	534·4 538.3	43 ² .7 438.6	325.0 333.4	223.4	145.3

We supposed here that the air of the cloud adiabat is just saturated with vapor at 1000 mb but does not contain liquid water. This point, + 18.5°C at 1000 mb, is the condensation point. We note that a cloud adiabat is not uniformly defined by means of only one temperature-pressure point through which it goes on the diagram, nor by means of the entropy sum $S_g + S_w$. It depends also on the total H_2O amount in the air and this varies with the condensation point. For an air parcel with given p_a , T, u without condensation products the cloud adiabat is,



of course, uniformly defined, but if we wish to draw on the diagram paper cloud adiabats without considering a given state of air we get an infinite group of curves through each point (p_a, T) , the different curves depending on the total water amount. — Each pseudo-adiabat is uniformly defined by one point (p_a, T) through which it goes.

Fig. 2 and the preceding table show that the cloud adiabat and the pseudo-adiabat follow very close to one another from the ground to a

height of about 4-5 kms and here we still have a case with a rather great H_2O amount. All the rain adiabats lie between these two. Thus, we can see that the use of one or the other of the infinitely many condensation adiabats is practically the same up to 4-6 km. — Because the pseudo-adiabats are uniformly defined curves on the thermodynamic diagram their use is well motivated. The reason why the cloud adiabat and the pseudo-adiabat so closely follow one another lies in the small difference of entropies for cloud water on the cloud adiabat and for the precipitated rain along the pseudo-adiabat, at the beginning of the curves.

Potential temperatures (see e.g. Bleeker [2]) used as conservative quantities in synoptic investigations are numerous. In fact, it is possible to define an infinite number of different potential temperatures using the infinite number of adiabats.¹)

If we use the entropy and (total) mixing ratio (m) as conservative quantities, we have in general

$$S = S(p_a, T, m_v, m_w, m_i) = s_a + S_v + S_w + S_i$$

 $m = m_v + m_w + m_i$

If we are able to measure or estimate the amounts m_w and m_i there are no difficulties in computing all the entropies and m. In the case of clear air, $m_w = m_i = o$, we have $S = s_a + S_v = S_g$. The entropy of water or ice in clouds amounts in the most unfavorable cases to about 25 J/° C, but in most cases it is much smaller. The accuracy of determining s_a and S_v is not better than \pm 1 J/° C, as a rule. In any case, the entropy of cloud water (and ice) should be taken into account. But so far this is practically impossible. Therefore we must be contented with computing the entropy of the gaseous parts, S_g , only. This agrees with the total entropy in clear air, i.e. in most cases.

We can not imagine the above named potential temperatures to afford any very important advantage when compared with entropies if one think not that a »temperature» is more familiar to be adapted for use than an entropy. But it seems to us that when compared with potential temperatures the entropy has some important properties: it is uniformly defined by general physical laws while the potential temperatures have been defined in many different ways; the entropies follow the simple law of additivity (3) but the different potential temperatures do not stand in such a simple relation to one another.

¹) Furthermore, the reference pressure 1 000 mb can be either total pressure (p) or partial pressure of dry air (p_a) . We have used the latter.

Taking in consideration a given state of clear air with the entropies S_a , S_v , $S_w = 0$, $S_i = 0$, $S_g = S_a + S_v$ we can say that

(20a) s_n corresponds to the (dry) potential temperature

(20b)
$$S_v$$
 » » dew point » » (20c) S_g » » wet-bulb »

(20c)
$$S_g$$
 » » wet-bulb » »

(20d)
$$S_q^{"}$$
 » » equivalent »

Between entropies and the potential temperatures there is only in the case (20a) a simple relation:

(21)
$$s_a = c_{ap} \ln \frac{\vartheta_a}{T_n} \text{ or } \vartheta_a = T_n e^{\frac{S_a}{C_{ap}}}.$$

The dew point temperature (τ) is determined by means of

(22)
$$E(\tau) = e = u E(T)$$

and the dew point potential temperature (ϑ_z) by means of

(23)
$$E(\vartheta_r) = u \frac{p_n}{p_n} E(T)$$

Referring to (13) we then get

(24)
$$E\left(\vartheta_{\tau}\right) = \frac{u}{u'} \frac{S_{v}}{\varepsilon \ \sigma(T)} \ p_{n}$$

Because $\frac{u}{r}$ differs only slightly from 1 and because $\sigma(T)$ also varies

only slightly with temperature (with 20°C the change of σ is about 5%) we see that ϑ_{τ} is nearly defined by means of S_n only. Neglecting T and u, the error in determining ϑ_{τ} is generally some tenths of a degree centigrade only.

As to the mixing ratio m_v compared with S_v we have

$$m_{\nu} = \frac{u}{u'} \frac{S_{\nu}}{\sigma(T)}$$

This relationship shows that on neglecting T and u, m_v is determined by means of S_v generally with an accuracy of some percents.

Isentropic potential temperatures. It is possible to define potential temperatures which are related to the many potential temperatures defined earlier but are uniform functions of entropies. There may be given a state of air: (p_a, T, u) in case of unsaturated (clear) air or (p_a, T, m_v, m_w, m_t) in case of cloud air. The entropies may be \bar{s}_a , \bar{S}_v , \bar{S}_w , \bar{S}_i , \bar{S}_g , \bar{S}_s . We define the following potential temperatures:

by means of the relations:

$$\begin{array}{lll} \text{(26a)} & s_{\alpha} \ (p_{n}, \ \vartheta_{a}) = \overline{s}_{\alpha} \\ \text{(26b)} & S_{\nu} \ (p_{n}, \ \vartheta_{\nu}, \ 1) = \overline{S}_{\nu} \ \text{resp.} = \overline{S}_{\nu} + \overline{S}_{\nu} + \overline{S}_{i} \\ \text{(26c)} & S_{g} \ (p_{n}, \ \vartheta_{s}, \ 1) = \overline{S}_{g} \quad \text{\Rightarrow} = \overline{S} \\ \text{(26d)} & s_{\alpha} \ (p_{n}, \ \vartheta_{e}) = \overline{S}_{g} \quad \text{\Rightarrow} = \overline{S}. \end{array}$$

These temperatures have the same properties of invariance as the entropies and are uniformly defined by means of the equations (26). They agree, with some accuracy, with the usual potential temperatures. If water and ice in the cloud are not measured or estimated they must be left off from the equations (26). ϑ_a is the usual potential temperature. — The argument 1 in (26b and c) means saturation, u=1.

Invariants. It can be shown that in adiabatic-processes of a closed-system not only the total mixing ratio (m) and the total entropy (S) but also s_a and $S(H_2O) = S_v + S_w + S_i$ remain constant with great accuracy. Therefore it seems acceptable to us to use instead of the total mixing ratio m the entropy of H_2O , namely $S_v + S_w + S_i$ as conservative quantity and further instead of total entropy (S) the partial entropy of dry air s_a . Then, because of the additivity (3), the total entropy is given by

(27)
$$S = s_a + S(H_2O).$$

The entropy of $\rm H_2O$ will also very well represent the mixing ratio and the partial entropy of dry air will describe the common potential temperature. If it is desired to draw curves of total entropy also they are, according to (27), diagonal curves of the two foregoing curves.

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