Atmospheric Thermodynamics

First Law of Thermodynamics

A system possesses macroscopic kinetic and potential energy as well as internal energy (u) due to the kinetic and potential energy of its molecules or atoms.

$q - w = u_2 - u_1$

where

q - thermal energy (heat) received by a system (J)
w - external work done by the system (J)
u_1, u_2 - internal energy of system before and after change (J)

Changes in internal kinetic energy are manifested as changes in temperature.

Changes in internal potential energy are caused by changes in the relative positions of molecules due to forces that act between the molecules.

This relationship can be expressed in differential form as:

$dq - dw = du$

where

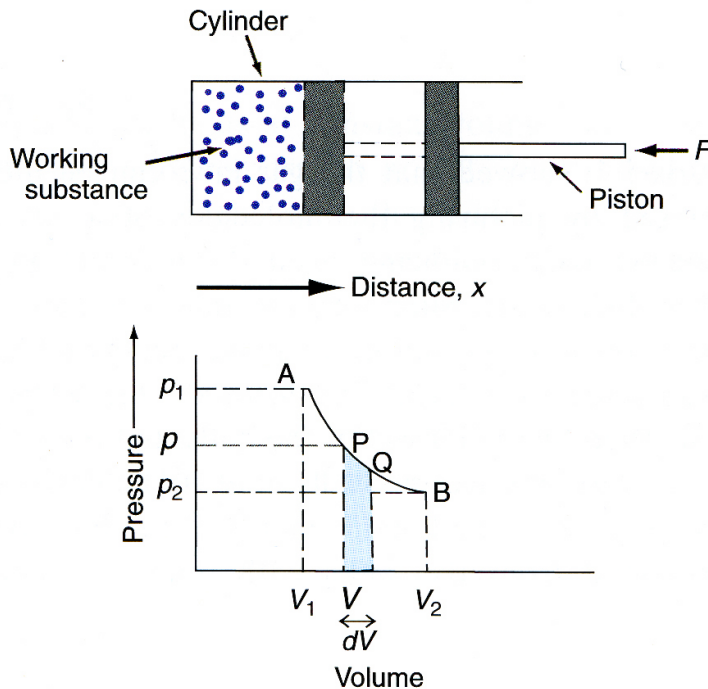dq - differential increment of heat added to the system
dw - differential increment of work done by the system
du - differential increase in internal energy of the system

Both of these equations are statements of the first law of thermodynamics.

Work done by a gas

Consider a gas contained in a cylinder that is fitted with a piston:

The volume (V) and pressure (p) exerted by the gas can be shown on a p-V diagram

If the gas expands (increase in V) it will push the piston a distance dx and will do an amount of work (dW) given by:

$$dW = Fdx$$

The force exerted by the gas is equal to pA (where A is the cross-sectional area of the piston).

$$dW = pAdx = pdV$$

The work done by the gas (dW) is equal to the pressure (p) exerted by the gas multiplied by the change in volume (dV) of the gas, and is indicated by the shaded area under the curve on the p-V diagram

When the gas passes from state A to state B the work done is given by:

$$\int dW = \int_{V_1}^{V_2} pdV$$

When $V_1 > V_2$ (the gas is compressed) work is done on the gas and $W<0$

When $V_2 > V_1$ (the gas expands) work is done by the gas and $W>0$

The work done in going from volume V_1 to volume V_2 depends on the path of integration and as such is not an exact differential.

Dividing by the mass of the gas gives the specific work:

$$\int dw = \int_{\alpha_1}^{\alpha_2} p d\alpha \text{ or } dw = p d\alpha$$

and the first law of thermodynamics is then expressed as:

$dq = du + p d\alpha$

Specific Heats

Specific heat: The ratio of the heat added to a system to the change in temperature of the system ($=dq/dT$)

The units for specific heat are J kg^{-1} K^{-1}

The value of the specific heat depends on how the material (gas) changes as heat is added.

Specific heat at constant volume (c_v)

$$c_v = \left(\frac{dq}{dT}\right)_{v \text{ const}}$$

At constant volume a gas does no work and the first law of thermodynamics reduces to $dq = du$

Then c_v can be expressed as:

$$c_v = \left(\frac{du}{dT}\right)_{v \text{ const}} \text{ and } du = c_v dT$$

Using this expression for c_v the first law of thermodynamics is:

$dq = c_v dT + p d\alpha$

Internal energy (*u*) is a function of state, and changes in internal energy depend only on the initial and final states and not on the path taken between these states.

Therefore: $\int_{u_1}^{u_2} du = u_2 - u_1 = \int_{T_1}^{T_2} c_v dT$

Specific heat at constant pressure (*c_p*)

Defined as: $c_p = \left(\dfrac{dq}{dT}\right)_{p\ \text{const}}$

In this case work is done by the gas, since as heat is added to the gas the gas expands (*dW = pdV*).

Therefore some of the heat added to the gas goes into doing work, and for a given change in temperature more heat must be added to a gas for a constant pressure process than for a constant volume process, and $c_p > c_v$

The relationship between c_v and c_p can be found by taking the first law of thermodynamics (*dq = c_v dT + pdα*)

and rewriting it as

dq = c_v dT + d(pα) - αdp

Combining this with the derivative of the ideal gas law (*pα = RT*):

d(pα) = d(RT) = RdT

gives

dq = c_v dT + RdT - αdp = (c_v + R)dT - αdp

For a constant pressure process $\alpha dp = 0$ and

$$\left(\frac{dq}{dT}\right)_{p \text{ const}} \equiv c_p = c_v + R$$

This can be used to express the first law of thermodynamics as

$dq = c_p dT - \alpha dp$

The value of c_p and c_v for dry air are:

$c_p = 1004$ J kg^{-1} K^{-1}

$c_v = 717$ J kg^{-1} K^{-1}

Enthalpy

Enthalpy is a function of state defined by:

$$h \equiv u + p\alpha$$

Since $u, p,$ and α are functions of state enthalpy is also a function of state.

Differentiating the definition of h gives:

$dh = du + d(p\alpha)$

Using $du = c_v dT$ and $dq = c_v dT + d(p\alpha) - \alpha dp$ gives

$dq = dh - \alpha dp$

which is another form of the first law of thermodynamics

From $dq = c_p dT - \alpha dp$ we see that

$dh = c_p dT$ and in integrated form $h = c_p T$

From this equation we note that h corresponds to the heat required to raise the temperature of a material from 0 to T K at constant pressure.

When heat is added to air at constant pressure

$dq = dh = c_p dT$

and the enthalpy increases. Enthalpy is also commonly referred to as sensible heat.

Special Processes

Referring to the first law of thermodynamics expressed as:

$dq = c_v dT + pd\alpha$

or

$dq = c_p dT - \alpha dp$

we can consider a number of special processes.

Isobaric process: $dp = 0$

$$dq = c_p dT = \left(\frac{c_p}{c_v}\right)c_v dT = \left(\frac{c_p}{c_v}\right)du$$

Isothermal process: $dT = 0$

$$dq = -\alpha dp = pd\alpha = dw$$
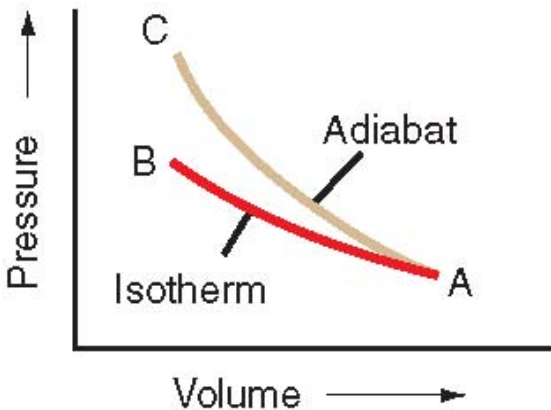
Isochoric process: $d\alpha = 0$

$$dq = c_v dT = du$$

Adiabatic process: *dq* = 0

$$c_p dT = \alpha dp$$

$$c_v dT = -p d\alpha$$

An adiabatic process is one in which a material undergoes a change in its physical state (e.g. pressure, volume, or temperature) without any heat being added to it or withdrawn from it.

Consider isothermal and adiabatic compression illustrated on a p-V diagram:

For both processes *V* and α decrease

For the isothermal process (shown by curve AB) this implies that *p* must increase

For the adiabatic process (shown by curve AC) the internal energy, and thus temperature, increases.

For the same mass of gas at the same volume (points B and C) the sample with the higher temperature (C) will also have a higher pressure, hence the adiabat (AC) on the p-V diagram is steeper than the isotherm (AB)

Air parcel – a small mass of air that is thermally insulated from its environment, such that its temperature changes adiabatically, and that has exactly the same pressure as its environment

Dry Adiabatic Lapse Rate

Consider an air parcel undergoing an adiabatic change in pressure, with no phase change of any water substance in the air parcel.

For this air parcel the first law of thermodynamics can be written as:

$$c_p dT = \alpha dp$$

$$c_p dT = \frac{RT}{p} dp$$

Since this change in pressure implies a change in elevation:

$$c_p \frac{dT}{dz} = \frac{RT}{p} \frac{dp}{dz}$$

From the hydrostatic equation:

$$\frac{dp}{dz} = -\rho g$$

Combining these equations give:

$$\frac{dT}{dz} = -\frac{\rho g RT}{c_p p}$$

$$= -\frac{g}{c_p}$$

$$= -\frac{-9.81 \text{ m s}^{-2}}{1004 \text{ J kg}^{-1} \text{ K}^{-1}}$$

$$= -9.8 \times 10^{-3} \text{ K m}^{-1}$$

$$= -9.8 \text{ K km}^{-1}$$

This decrease in temperature with altitude is referred to as the dry adiabatic lapse rate (Γ_d)

$$\Gamma_d \equiv -\left(\frac{dT}{dz}\right)_{\text{dry parcel}} = \frac{g}{c_p} = 9.8 \text{ K km}^{-1}$$

In general a lapse rate (Γ) always refers to the rate of decrease of temperature with height $\left(-\dfrac{dT}{dz}\right)$.

The lapse rate in a column of air (referred to as the environmental lapse rate) need not be equal to the dry adiabatic lapse rate and typically averages 6-7 K km^{-1} in the troposphere.

What is the sign of the lapse rate if:

T decreases with height?

T increases with height?

T is constant with height?

Potential Temperature (θ) - the temperature an air parcel would have if it were expanded or compressed adiabatically from its existing pressure and temperature to a standard pressure p_0 (=1000 hPa)

An expression for potential temperature can be derived by considering the first law of thermodynamics for an adiabatic ($dq = 0$) process:

$$c_p dT = \alpha dp$$

Using the ideal gas law to replace α gives:

$$c_p dT = RT\frac{dp}{p}$$

$$\frac{c_p}{R}\frac{dT}{T} = \frac{dp}{p}$$

This expression can be integrated from p_0, where $T_0 = \theta$ by definition, to p (and T):

$$\int_{\theta}^{T} \frac{c_p}{R} \frac{dT}{T} = \int_{p_0}^{p} \frac{dp}{p}$$

$$\frac{c_p}{R} \ln \frac{T}{\theta} = \ln \frac{p}{p_0}$$

$$\left(\frac{T}{\theta}\right)^{\frac{c_p}{R}} = \frac{p}{p_0}$$

$$\theta = T \left(\frac{p_0}{p}\right)^{\frac{R}{c_p}}$$

This equation for potential temperature is known as Poisson's equation.

For an adiabatic process the potential temperature of an air parcel is conserved (i.e. it remains constant).

Typically this equation is applied to dry air, so $R = R_d$ and $c_p = c_{pd}$.

This gives:

$$\frac{R}{c_p} = \frac{R_d}{c_{pd}} = \frac{287 \text{ J kg}^{-1} \text{ K}^{-1}}{1004 \text{ J kg}^{-1} \text{ K}^{-1}} = 0.286$$

Example: What is the potential temperature at the ATOC weather station?

How does the pressure, temperature, and potential temperature of an air parcel change if the air parcel is lifted adiabatically in the atmosphere?

Adiabatic cooling and adiabatic warming

Example: What would the temperature of an air parcel be if it were lifted from the ATOC weather station to Nederland by an adiabatic process?

Thermodynamic Diagrams

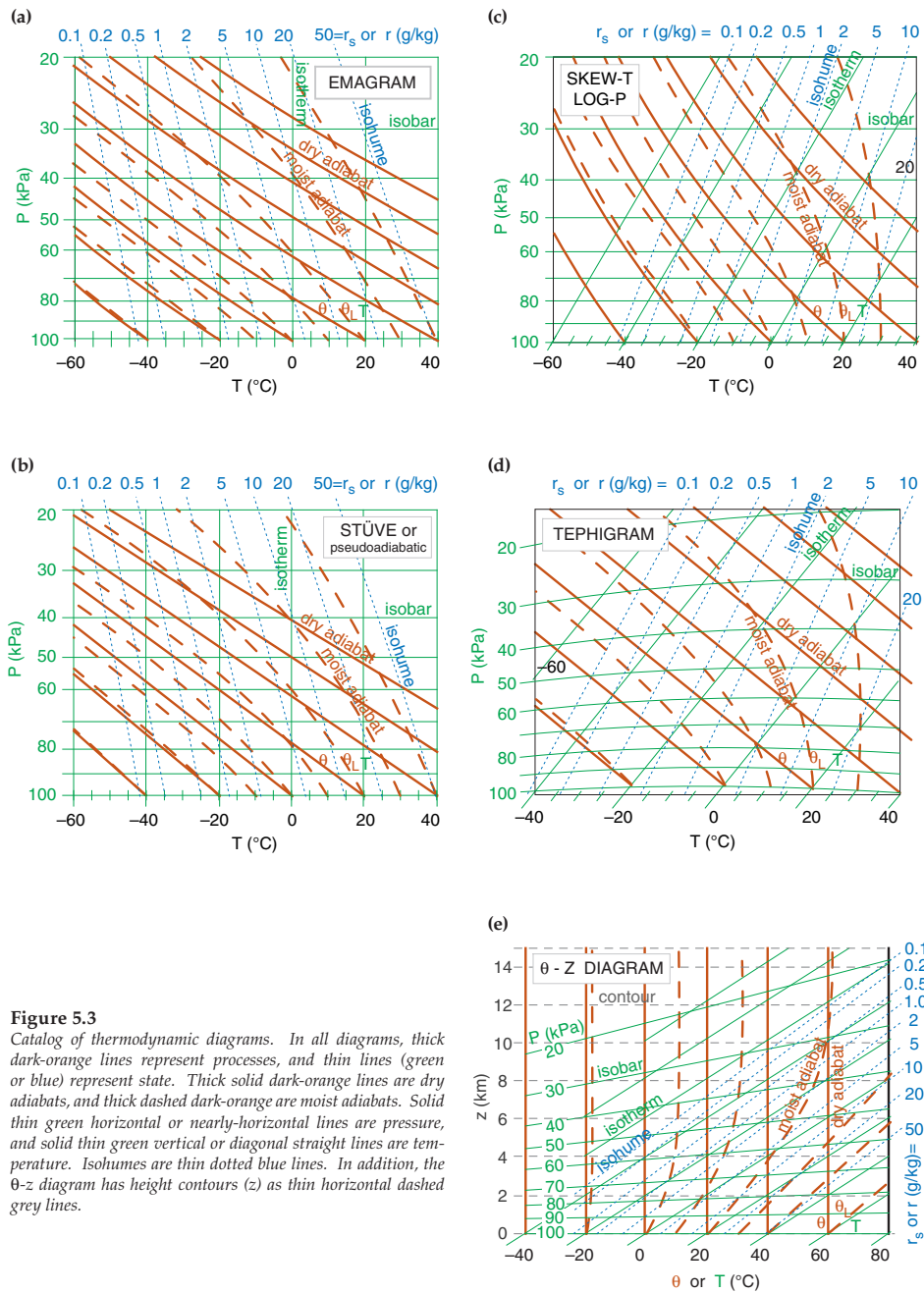Thermodynamic diagram - a chart whose coordinates are variables of state

Figure 5.3

Catalog of thermodynamic diagrams. In all diagrams, thick dark-orange lines represent processes, and thin lines (green or blue) represent state. Thick solid dark-orange lines are dry adiabats, and thick dashed dark-orange are moist adiabats. Solid thin green horizontal or nearly-horizontal lines are pressure, and solid thin green vertical or diagonal straight lines are temperature. Isohumes are thin dotted blue lines. In addition, the θ-z diagram has height contours (z) as thin horizontal dashed grey lines.
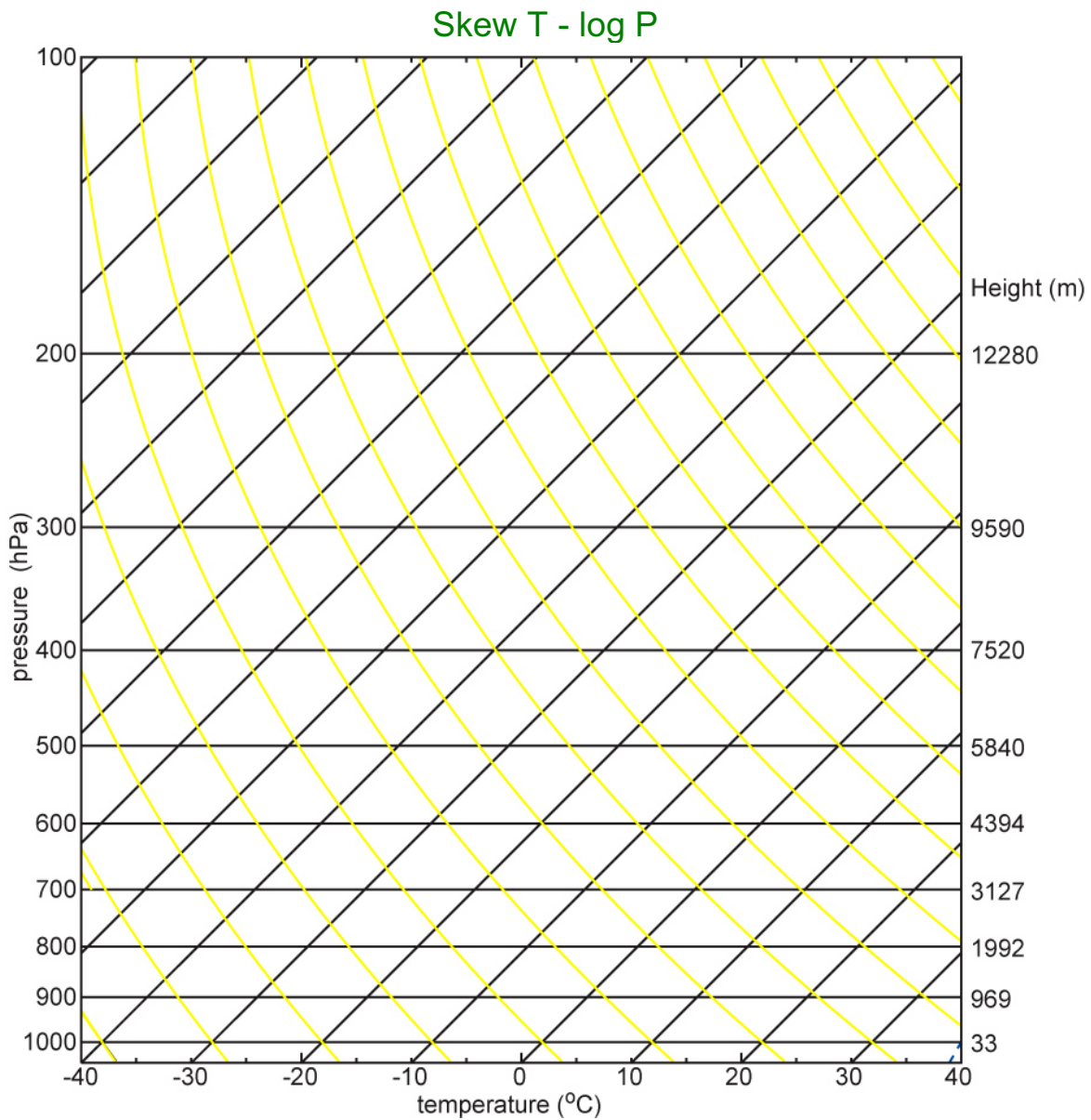
Skew T - log P

Information plotted on a dry skew T – log p diagram:

Pressure: black horizontal lines (Units: hPa or mb) (logarithm of pressure is used as the vertical axis on this diagram)

Temperature: Black lines that slope up and to the right (units: °C)

Dry adiabat: Lines of constant potential temperature – curved yellow lines that slope up and to the left (Units: °C)

Example: Plot weather observations from ATOC weather station on a skew
T - log P diagram.
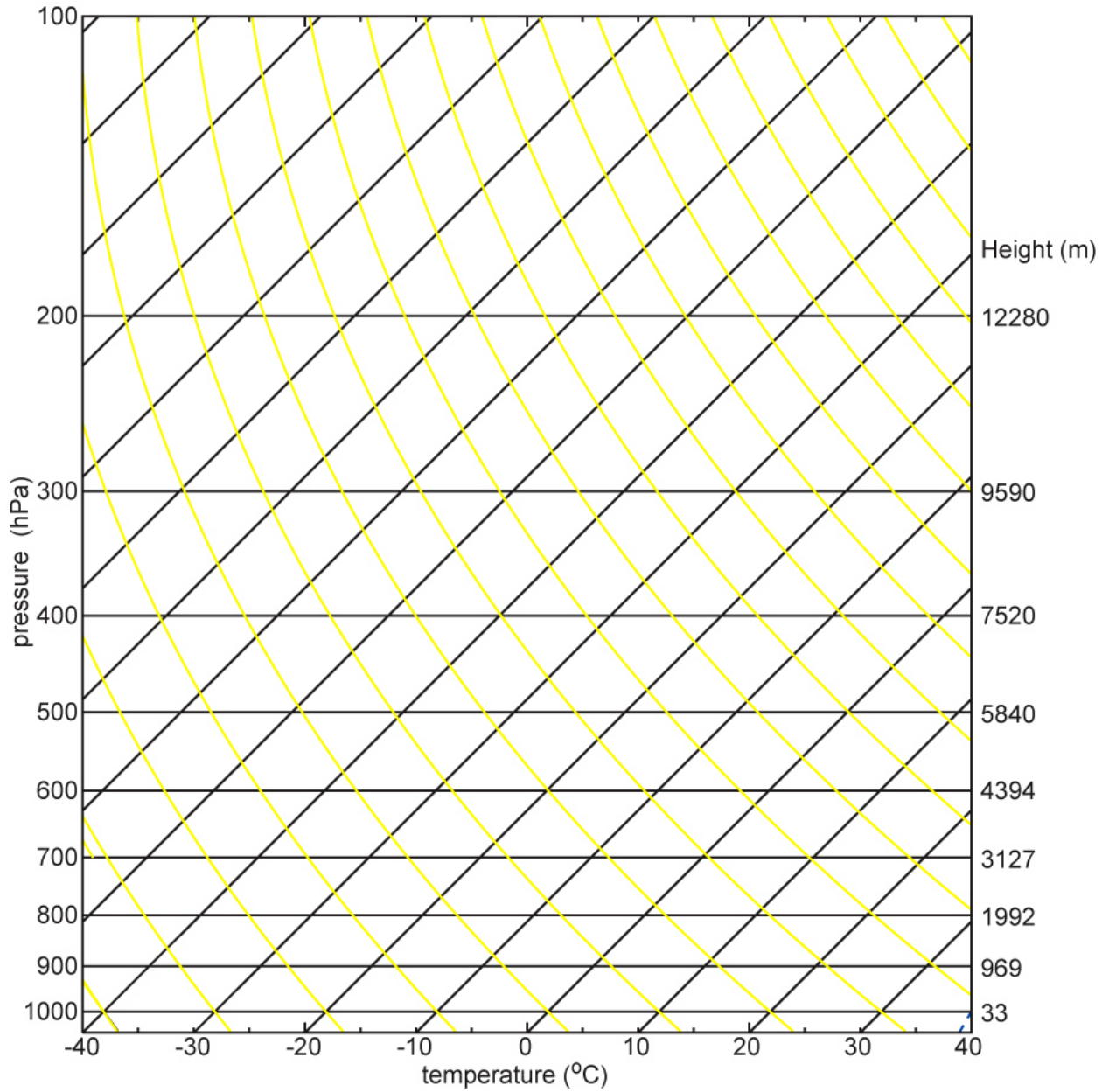
Real-time example: Stüve and Skew T soundings