Evaporation and precipitation of water

Exercises Accompanying the Course Reaction Transport Modelling in the Hydrosphere

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Abstract

Consider a water body surrounded by air. If the relative humidity of the air is below 100%, water will evaporate. In contrast, if the relative air humidity exceeds 100%, which occurs, for instance, when air with a given water vapor content cools down, water will precipitate from the gas phase to form a liquid. In both cases, the process will continue until an equilibrium is reached, i.e., until the relative humidity reaches 100%. In this reader, we will show how these processes can be modeled in R.

Theoretical background

Consider a closed container filled with water and air (Figure 1). The volume and amount of water in the liquid phase are V_{liq} (m^3) and N_{liq} (mol), respectively. The gas phase has a volume V_{gas} and contains a mixture of air (amount N_{air}) and water vapor (amount N_{vap}). The liquid water can evaporate to form water vapor, and vice versa, water vapor can precipitate to form liquid water. These processes occur across the liquid-gas boundary (area A_{liq}).

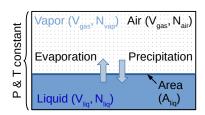


Figure 1: Gas-tight container filled with liquid water and moist air.

In the first approximation, precipitation is assumed to be described by first-order kinetics, i.e., the rate is linearly proportional to N_{vap} (more specifically to the concentration of water vapor molecules, N_{vap}/V_{gas}), whereas evaporation is assumed to follow zero-order kinetics, i.e., the rate is independent of N_{vap} (as long as the liquid water is present). Additionally, because the exchange of water molecules occurs at the interface between the liquid and gas phase, both rates are assumed to be proportional to A_{liq} . Thus, the change over time in the number of water vapor molecules above the liquid is described by the following differential equation:

$$\frac{dN_{vap}}{dt} = k_f \cdot A_{liq} - k_b \cdot A_{liq} \cdot \frac{N_{vap}}{V_{qas}},\tag{1}$$

where the rate constants k_f (in $mol\ m^{-2}\ s^{-1}$) and k_b (in $m\ s^{-1}$) correspond to the forward (evaporation) and backward (precipitation) reaction, respectively. Considering that the system is closed, the total amount of water molecules must be conserved. Thus, the amount of molecules of liquid water changes over time at the same rate as the amount of vapor molecules but with the opposite sign:

$$\frac{dN_{liq}}{dt} = -\frac{dN_{vap}}{dt}. (2)$$

When the time derivative dN_{vap}/dt is equal to zero, the system reaches an equilibrium. Equation 1 implies that the corresponding equilibrium concentration of vapor molecules is equal to the ratio between the rate constants for the forward and backward reaction:¹

$$\frac{dN_{liq}}{dt} = 0 \quad \to \quad \left(\frac{N_{vap}}{V_{qas}}\right)^* = \frac{k_f}{k_b}. \tag{3}$$

Using this equilibrium concentration, Eq. 1 can be rewritten in the following form:

$$\frac{dN_{liq}}{dt} = -\frac{dN_{vap}}{dt} = k_b \cdot A_{liq} \cdot \left[\left(\frac{N_{vap}}{V_{gas}} \right)^* - \left(\frac{N_{vap}}{V_{gas}} \right) \right]. \tag{4}$$

Thus, the process of evaporation and precipitation can be thought of as being driven by a chemical disequilibrium, i.e., the net rate of exchange of water molecules between the liquid and gas phase is proportional to the difference between the equilibrium and instantaneous concentration of vapor molecules above the liquid.

Reformulation of the equations using vapor pressure

If water vapor behaves as an ideal gas, the concentration of water vapor molecules is related to the vapor pressure, P_{vap} , through the ideal gas law,

$$\frac{N_{vap}}{V_{qas}} = \frac{P_{vap}}{R \cdot T},\tag{5}$$

where $R = 8.314 \ J \ K^{-1} \ mol^{-1}$ is the gas constant, and T is the vapor temperature (in K). Using this relationship, Eq. 4 can be rewritten in the form

$$\frac{dN_{vap}}{dt} = \frac{k_b}{R \cdot T} \cdot A_{liq} \cdot \left(P_{vap}^* - P_{vap}\right),\tag{6}$$

where P_{vap}^* denotes the equilibrium vapor pressure.² This form is equivalent to the empirical relationship developed by Carrier (1918) to describe water evaporation and precipitation:

$$\frac{dN_{vap}}{dt} = \frac{c_1 + c_2 \cdot v}{\Delta \bar{H}_{vap}} \cdot A_{liq} \cdot \left(P_{vap}^* - P_{vap}\right),\tag{7}$$

where $\Delta \bar{H}_{vap}$ is the molar enthalpy of vaporization of water ($\approx 40.66~kJ~mol^{-1}$), v is the wind velocity (in $m~s^{-1}$), and $c_1 = 0.0888~m~s^{-1}$ and $c_2 = 0.0783$ are empirical constants.

By comparing Eqs. 6 and 7, we see that the precipitation rate constant k_b in Eq. 1 can be calculated from the empirical constants c_1 and c_2 according to

$$k_b = \frac{R \cdot T}{\Delta \bar{H}_{vap}} \cdot (c_1 + c_2 \cdot v). \tag{8}$$

Additionally, by combining this result with Eqs. 3 and 5, the evaporation rate constant k_f in Eq. 1 can be calculated from k_b , temperature, and the equilibrium vapor pressure according to

$$k_f = k_b \cdot \frac{P_{vap}^*}{R \cdot T}.\tag{9}$$

Equilibrium vapor pressure

The equilibrium vapor pressure depends on the temperature of the system comprising liquid water and water vapor and can be calculated if the temperature is known. For example, we know that water boils at

¹In this document, values of variables in a thermodynamic equilibrium are marked with an asterisk (*).

 $^{{}^{2}}P_{vap}^{*}$ is related to the equilibrium concentration $(N_{vap}/V_{gas})^{*}$ through the ideal gas law (Eq. 5).

a temperature of 100 °C when the external pressure is 1 atm. Thus, the equilibrium vapor pressure at a temperature of $T_{boil} = 373.15 \ K$ is $P_{vap}^*(T_{boil}) = 1 \ atm = 101325 \ Pa$. At any other temperature, T, the equilibrium vapor pressure is calculated using the Clausius-Clapeyron equation:

$$\ln\left[\frac{P_{vap}^{*}(T)}{P_{vap}^{*}(T_{boil})}\right] = -\frac{\Delta \bar{H}_{vap}}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{boil}}\right). \tag{10}$$

This result follows from equilibrium thermodynamics and assumes that the molar enthalpy of vaporisation of water, $\Delta \bar{H}_{vap}$, is temperature-independent.

Molar fraction and partial pressure

When dealing with mixtures, properties of individual components in the mixture are described by $partial \ molar$ quantities. One of the most basic partial molar quantities is $molar \ fraction$, typically denoted by x. For a component A, this quantity is defined as the ratio between the amount of component A and the total amount of the mixture (both amounts are in moles):

$$x_A = N_A/N_{tot} \quad (mol \ mol^{-1}). \tag{11}$$

When dealing with gas mixtures, such as atmospheric air, individual components are typically characterized by another quantity: partial pressure. If a mixture behaves as an ideal gas, partial pressures are additive. Thus, partial pressure of an individual component is equal to the product of the total pressure, P_{tot} , and the molar fraction of that component: $P_A = x_A \cdot P_{tot}$. Because moist air at typical conditions behaves as an ideal gas, partial pressure of water vapor is calculated as

$$P_{vap} = x_{vap} \cdot P_{air}, \tag{12}$$

where x_{vap} is the molar fraction of water vapor in air and P_{air} is the total air pressure. For example, if the total air pressure is 1 atm and 1 in every 1000 molecules of air is water, the molar fraction of water vapor is $x_{vap} = 0.001$ and the corresponding partial pressure of water vapor is $P_{vap} = 1$ matm.

Relative air humidity

Rather than using a molar fraction, the water content of air is very often expressed in terms of a *relative humidity*, ϕ . This quantity is defined as the ratio between the vapor pressure and the equilibrium vapor pressure. Thus, if the relative humidity of air is known, the vapor pressure is calculated according to

$$P_{vap} = \phi \cdot P_{vap}^*. \tag{13}$$

Because the molar fraction of water vapor in air and the relative humidity of air are relative quantities, they are often expressed in %. This can cause confusion. We emphasize here that these two quantities are fundamentally different: while the molar fraction of water vapor in air is the ratio between the vapor pressure and the *total* air pressure (Eq. 12), the relative humidity of air is the ratio between the vapor pressure and the *equilibrium* vapor pressure (Eq. 13).

Task 1

Calculate the equilibrium vapor pressure, P_{vap}^* , for temperatures of 10 °C, 20 °C, and 50 °C. What are the corresponding vapor pressures, P_{vap} , and molar fractions, x_{vap} , if the total air pressure is 0.95 atm and the relative air humidity is 80 %?

Task 2

Consider a closed container filled with liquid water and moist air (Figure 1). Initially, the volume of the liquid water is $V_{liq} = 1 L$, the total volume of the container $(V_{liq} + V_{gas})$ is $1 m^3$, and the relative air humidity is 0 % (dry air). The system is kept at a constant temperature of $20 \degree C$ for 0.5 hr. Then, the system is cooled and kept at a constant temperature of $10 \degree C$ for another 0.5 hr. Through the entire process the system is kept at a constant pressure of 1 atm.

- Write a model that calculates the amount of water vapor above the liquid water as a function of time. Express this amount in moles, as a molar fraction, and as a relative air humidity.
- Evaluate the gross and net amounts of water transferred between the liquid and gas phase during the first and second half-hour intervals.

Assumptions

- Area of the liquid water surface is constant $(A_{liq} = 1 \ m^2)$.
- Air is stagnant. Thus, you can assume the wind velocity of v = 0 (see Eq. 7 and 8).
- Dissolution in water of air components such as N_2 or O_2 can be ignored.
- The air and water vapor behave as an ideal gas. Since the total pressure of the gas phase and the temperature of the entire system are kept constant, the evaporation and precipitation processes as well as the isobaric cooling phase will lead to a volume change for the liquid water, the gas phase (air + water vapor), as well as the total volume (liquid + gas phase). Except for the change in volume of the liquid water during cooling, these changes cannot be neglected. You can assume that the walls of the container are flexible to allow for such changes to occur without the need to perform an extra work.
- To evaporate N moles of water at a constant pressure and temperature, a certain amount of heat is required $(q = N \cdot \Delta \bar{H}_{vap})$. You can assume that this heat is supplied externally such that the pressure and temperature of the system can remain constant during the modeled time interval. Similarly, you can assume that the heat produced during precipitation is transferred to the surrounding. The cooling from 20 °C to 10 °C is also done by transferring heat to the surrounding.
- The liquid and gas phases are well mixed (i.e., homogeneous). Thus, you can ignore transport processes and base your model entirely on mass balances (Eqs. 1 and 2) and the ideal gas law (Eq. 5).

Task 1 — solution

First, we implement the Clausius-Clapeyron equation (Eq. 10) to calculate the equilibrium vapor pressure, then use Eq. 13 to calculate the vapor pressure, and finally use Eq. 12 to calculate the molar fraction.

```
# implement Clausius-Clapeyron equation
Peg vapor <- function(TK=300) # input temperature in K!</pre>
  101325 * exp(-40.66e3/8.314 * (1/TK - 1/373.15))
# conditions
Pair <- 0.95*101325
                                # air pressure, in Pa
humid <- 0.8
                                # relative air humidity
TK
      < c(10, 20, 50) + 273.15 # temperature, in K
     <- Peq_vapor(TK)</pre>
                                # equilibrium vapor pressure, in Pa
Pvap <- humid*Peq
                                 # vapor pressure, in Pa
xvap <- Pvap/Pair</pre>
                                 # molar fraction of water vapor
# display results as a data.frame
data.frame(T_K = TK, Peq_Pascal = Peq, xvap_percent = xvap*100)
##
        T_K Peq_Pascal xvap_percent
## 1 283.15
              1572.268
                           1.306702
## 2 293.15
              2834.040
                           2.355352
## 3 323.15 13335.969
                          11.083434
```

The above results show that although the relative air humidity is constant, the molar fraction of water vapor steeply increases with temperature from about 1 % to about 11 %. This increase is caused by the steep increase in the equilibrium vapor pressure with temperature.

Task 2 — solution

Model implementation in R

First, we define model parameters and empirical constants.

```
# model parameters
Aliq
         <- 1
                        # liquid water area (m2)
         <- 101325
                        # total pressure (Pa)
Ptot
         <- 0
                        # wind speed (m h-1)
v
                        # temperature during first period (K)
TK1
         <- 293.15
TK2
         <- 283.15
                        # temperature during second period (K)
# empirical constants or parameters
         <- 8.314
                        # qas constant (J mol-1 K-1)
Rgas
                        # molar enthalpy of vaporisation of water (J mol-1)
         <- 40.66e3
dHvap
c1
         <- 0.0888*3600 # empirical constant in Eq. 7 (m h-1)
c2
         <- 0.0783
                        # empirical constant in Eq. 7 (-)
rho
         <- 1e3
                        # water density (kg m-3)
MW
         <- 18e-3
                        # molar weight of water (kg mol-1)
```

Then, we define auxiliary functions for calculating the amounts of water molecules from the volume of the water vapor and liquid, respectively, and the rate constants from the temperature. We use the Peq_vapor() function defined above.

```
Nwater_vapor <- function(humid, TK, V){ # calculate Nvap from volume, T, and humidity
 humid*Peq_vapor(TK)*V/(TK*Rgas)
                                       # based on the ideal gas law (Eq. 5) and Eq. 13
}
Nwater_liquid <- function(V){</pre>
                                        # calculate Nlig from volume
 rho*V/MW
                                         # using density and molar weight
}
kbT <- function(TK, v=0){
                                        # rate constant of water precipitation (m h-1)
  Rgas*TK/dHvap*(c1+c2*v)
                                        # Eq. 8
kfT <- function(TK, v=0){</pre>
                                         # rate constant of water evaporation (mol m-2 h-1)
 kbT(TK, v) * Peq_vapor(TK)/(Rgas*TK) # Eq. 9
```

Finally, we define the model function based on the differential equations 1 and 2.

```
WaterEvapPrecip <-function(t, state, pars) {</pre>
 with (as.list(c(state, pars)),{
    # rate constants at the given temperature (TK given in pars)
   kb <- kbT(TK)
   kf <- kfT(TK)
   # volume of the gas phase (air+vapor) at a given Nvap, Nair, TK, and Ptot
    # (Nair given in pars)
   Vgas <- Rgas*TK*(Nair+Nvap)/Ptot # based on the ideal gas law</pre>
   # process rates, mol h-1, Eq. 1
   evaporation <- kf*Aliq
   precipitation <- kb*Aliq * Nvap/Vgas</pre>
   # time-derivatives
   dNvap.dt <- evaporation - precipitation</pre>
   dNlig.dt <- -evaporation + precipitation
   # extra output quantities
   Pvap <- Nvap/Vgas * Rgas * TK # partial pressure of vapor, Eq. 5
   Pair <- Nair/Vgas * Rgas * TK # partial pressure of air
   Pgas <- Pvap + Pair
                               # total pressure of the gas phase
   humid <- Pvap/Peq_vapor(TK) # relative air humidity, Eq. 13</pre>
   Vtot <- Vgas + Vliq
                               # total volume (liquid + gas)
   # return time-derivatives and ordinary variables as a list
   list(c(dNvap.dt, dNliq.dt),
        # extra output:
        # amounts of molecules
                                              # water, total
        Nwater = Nvap + Nliq,
        Nair = Ptot * Vgas/(Rgas*TK) - Nvap, # air, total (to check!)
        # process rates, mol h-1
```

```
R.evaporation = evaporation,
       R.precipitation = precipitation,
       # rate constants
                          \# m h-1
       kb = kb.
       kf = kf,
                         # mol m-2 h-1
       # volumes, m3
       Vgas = Vgas,
                          # gas phase
                          # liquid phase
       Vliq = Vliq,
       Vtot = Vtot,
                          # total (qas+liquid)
       # pressures, Pa
       Pvap = Pvap, # partial pressure of vapor
       Pair = Pair, # partial pressure of air
       Pgas = Pgas, # total qas pressure (vapor+air)
       # fractions
       xvap = Nvap/(Nvap+Nair), # molar fraction of water vapor in air, Eq. 11
       #xvap = Pvap/Pext, # molar fraction of water vapor in air, Eq. 12
       humid = humid
                             # relative air humidity, (-)
})
```

Model application

Initial conditions and run 1

First, we define a function that returns the values of state variables (i.e., initial amounts of water vapor and liquid water molecules) and model parameters (i.e., temperature and amount of air molecules) based on the conditions defined by the problem (i.e., initial total volume, initial volume of the liquid water, initial relative air humidity, and initial temperature).

Now, we use the above function to generate the initial conditions and model parameters and solve the model over the first half-hour.

```
# initial conditions
Vtot.ini <- 1; Vliq.ini <- 1e-3; humid.ini <- 0
ini <- find_state_pars(Vtot=Vtot.ini, Vliq=Vliq.ini, humid=humid.ini, TK=TK1)</pre>
```

```
# solve the model over the first half-hour
outtimes <- seq(from = 0, to = 0.5, length.out = 400) # time in hr
require(deSolve)
out1 <- ode(y = ini$SV, parms = ini$pars, func = WaterEvapPrecip, times = outtimes)</pre>
```

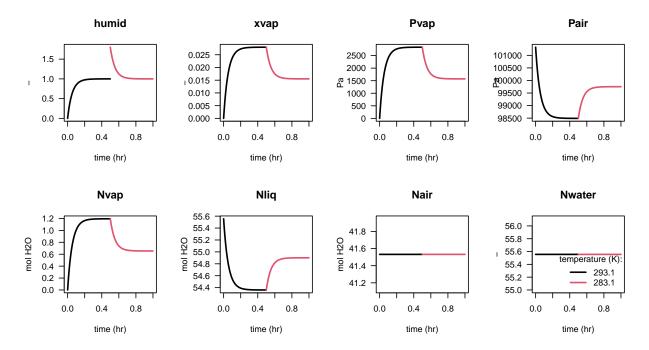
New initial conditions and run 2

In the second step, we use the end values of the first model run to calculate the initial conditions for the second model run. The gas was cooled from T_1 to T_2 at a constant pressure. Thus, the pressures do not change (this is true for the total pressure as well as for the partial pressures of the components in the gas phase). However, the volume of the gas phases decreases by a factor T_2/T_1 , as follows from the ideal gas law. Also, the equilibrium pressure decreases and, subsequently, the relative humidity increases as a result of the cooling. The change in the volume of the liquid water due to cooling is neglected (see Assumptions).

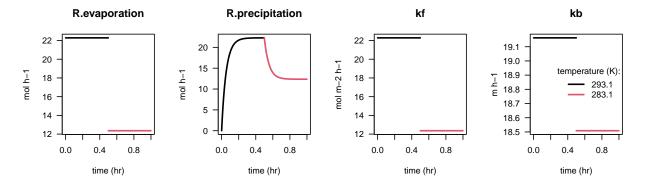
Results & Discussion

The first set of graphs (see below) shows that, due to net evaporation at the higher (initial) temperature, the relative air humidity increases from the initial 0 % to 100 % within about 15 minutes. This is associated with an increase in the molar fraction (from 0 to 0.028), vapor pressure (from 0 Pa to 2800 Pa) and a transfer of about 1.2 moles of water from the liquid to the gas phase.

The cooling of the 100 % humid air after 30 min increases the relative air humidity to about 180 %, leading to net precipitation. The new equilibrium is reached, again, in about 15 minutes, but the total changes in x_{vap} , P_{vap} , and N_{vap} are smaller.

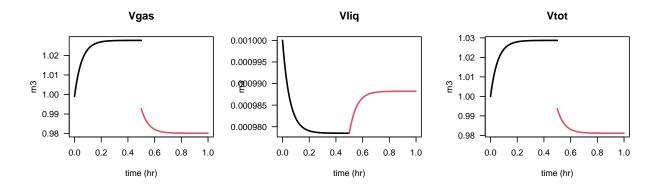


The second set of graphs (see below) shows that evaporation occurs at a rate of about 22.3 $mol\ h^{-1}$ and 12.4 $mol\ h^{-1}$ at the higher and lower temperature, respectively. During the first and second half-hour period, the precipitation rate increases and decreases towards the evaporation rate, respectively, reaching the level in about 15 minutes. Rate constants remain constant during each half-hour interval because the temperature is constant, but the values differ for the different temperatures (see Eqs. 8 and 9, where c_1 and c_2 are assumed to be temperature-independent).



The third set of graphs (see below) shows that, due to net evaporation at the higher (initial) temperature, the volume of the gas phase (air + water vapor) increases by about 28.74 L and the volume of the liquid water decreases by 21.5 mL. Thus, the overall volume of the system increases by about 28.72 L. Because the total pressure is constant, these changes are associated with an increase in the vapor pressure but a

decrease in the air pressure (i.e., pressure of air components other than the water vapor; see Pvap and Pair in the first set of graphs). The trends are opposite at the lower temperature during the second half-hour. The isobaric cooling in between the two half-hour intervals has a similar effect on the gas and total volumes as the evaporation/precipitation, but no effect on the liquid volume (as assumed).



Water budgets

Finally, we construct the water budgets by integrating³ the evaporation and precipitation rates over time, which yields *gross* amounts of evaporated and precipitated water, respectively. We also calculate the net amount of evaporated water as the difference in the gross amounts, which should be equal to the difference in the final and initial amounts of water vapor (it is). We also convert the amounts to volumes of liquid water, which are easier to imagine.

```
require(oce)
evap <- integrateTrapezoid(outtimes, out1[,"R.evaporation"])</pre>
                                                                    # gross amount evaporated
prec <- integrateTrapezoid(outtimes, out1[,"R.precipitation"]) # gross amount precipitated</pre>
                                                                    # difference final - initial
     <- diff(out1[c(1,nrow(out1)),"Nvap"])</pre>
# water budget in moles
(budget_mol <- c(evap=evap, prec=prec, net=evap-prec, net2=dN))</pre>
                                        net2
        evap
                   prec
                               net
## 11.140998 9.946012
                         1.194986
                                    1.194931
# water budget in milliliters
(budget_ml <- budget_mol*MW/rho * 1e6)
##
        evap
                   prec
                               net
                                        net2
## 200.53797 179.02821
                         21.50975
                                    21.50876
```

The above results show that, when going from 0 % to 100 % humid air at 20 $^{\circ}C$, about 11.14 and 9.95 moles of water is evaporated and precipitated, respectively, whereas the net increase in the amount of water vapor is only 1.19 mol. These amounts correspond to 201 mL of water evaporated, 179 mL of water precipitated, and 22 mL of net-evaporated water. Thus, the **gross** exchange of water between the liquid and gas phase is about 10-fold larger than the **net** increase in water vapor. Moreover, for an initial setup consisting of 1 L of liquid water surrounded by 999 L of air with a relative humidity of 0 % (surface area of 1 m^2), about 20 % of water evaporates, 18 % of water precipitates, and 2 % of the liquid water eventually ends up as water vapor within about 15 minutes.

 $^{^3}$ We use the "integrateTrapezoid" function from the "oce" package to perform the integration.

For completeness, we also construct a similar water budget for the second half-hour.

```
require(oce)
evap <- integrateTrapezoid(outtimes, out2[,"R.evaporation"])  # gross amount evaporated
prec <- integrateTrapezoid(outtimes, out2[,"R.precipitation"])  # gross amount precipitated
dN <- diff(out2[c(1,nrow(out2)),"Nvap"])  # difference final - initial

# water budget in milliliters
(budget_ml2 <- c(evap=evap, prec=prec, net=evap-prec, net2=dN)*MW/rho * 1e6)

## evap prec net net2
## 111.254421 120.979656 -9.725235 -9.724834</pre>
```

Thus, the decrease in temperature from 20 $^{\circ}C$ to 10 $^{\circ}C$ resulted in about 121 mL of water precipitated, 111 mL of water evaporated, and 10 mL of water net-precipitated.

Conclusion

The model results illustrate that much more water evaporation and precipitation occurs than "meets the eye"! The exchange occurs on the time-scale of minutes, consistent with our daily experience.

References

R Core Team (2020). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/.

Karline Soetaert, Thomas Petzoldt, R. Woodrow Setzer (2010). Solving Differential Equations in R: Package deSolve. Journal of Statistical Software, 33(9), 1–25. URL http://www.jstatsoft.org/v33/i09/ DOI $10.18637/\mathrm{jss.v033.i09}$

Carrier W. H. (1918). "The Temperature of Evaporation," Trans. Am. Soc. Heat. Vent. Eng., vol. 24, p. 25.