The Course of Atmospheric Thermodynamics

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SECOND STAGE
LECTURE 7

THIS LECTURE INCLUDING THE FOLLOWING ITEMS

- Phase Change

- Recall some terms that we learned in the first course of “Fundamentals of Thermodynamics”

- Entropy

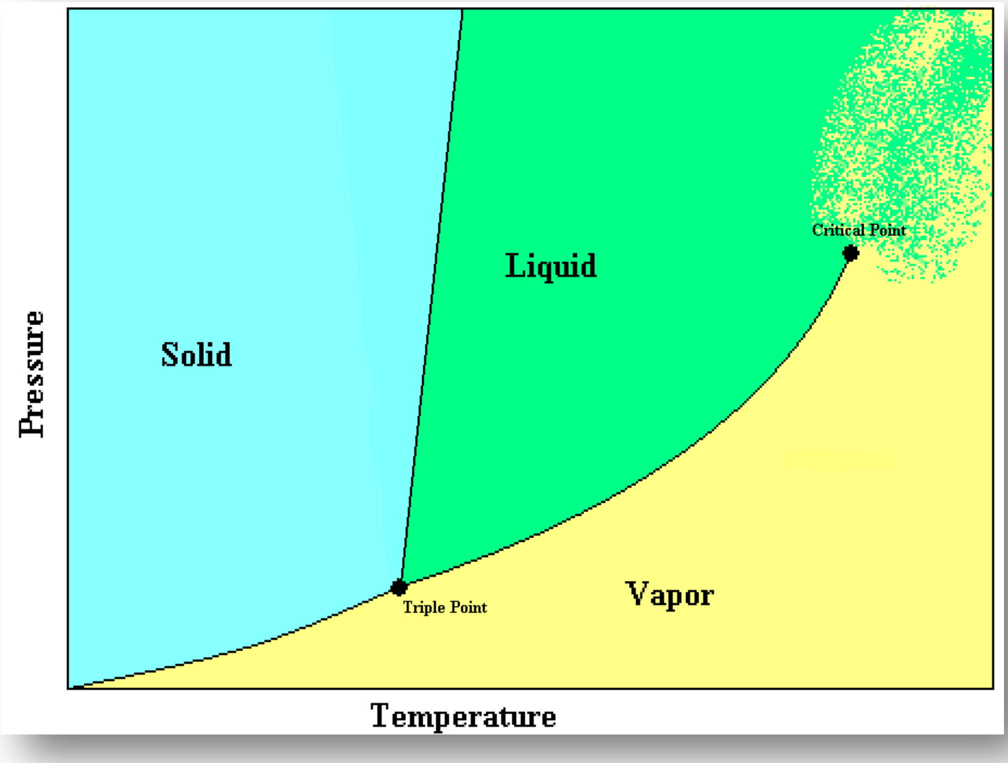
PHASE CHANGE

- Water vapor is an invisible gas that becomes visible when it changes into larger liquid or solid (ice) particles.
- This process of transformation is known as a **change of state or, simply, a phase change**.
- The heat energy required to change a substance, such as water, from one state to another is called **latent heat**.

- **But why is this heat referred to as “latent”?**

PHASE CHANGE

- A phase change is a change between solid, liquid, or vapor (gas).
- A system may even have more than one solid or liquid phase such as Carbon with two solid phases (graphite & diamond).
- The phase of a system in equilibrium can be represented on a **phase diagram**.

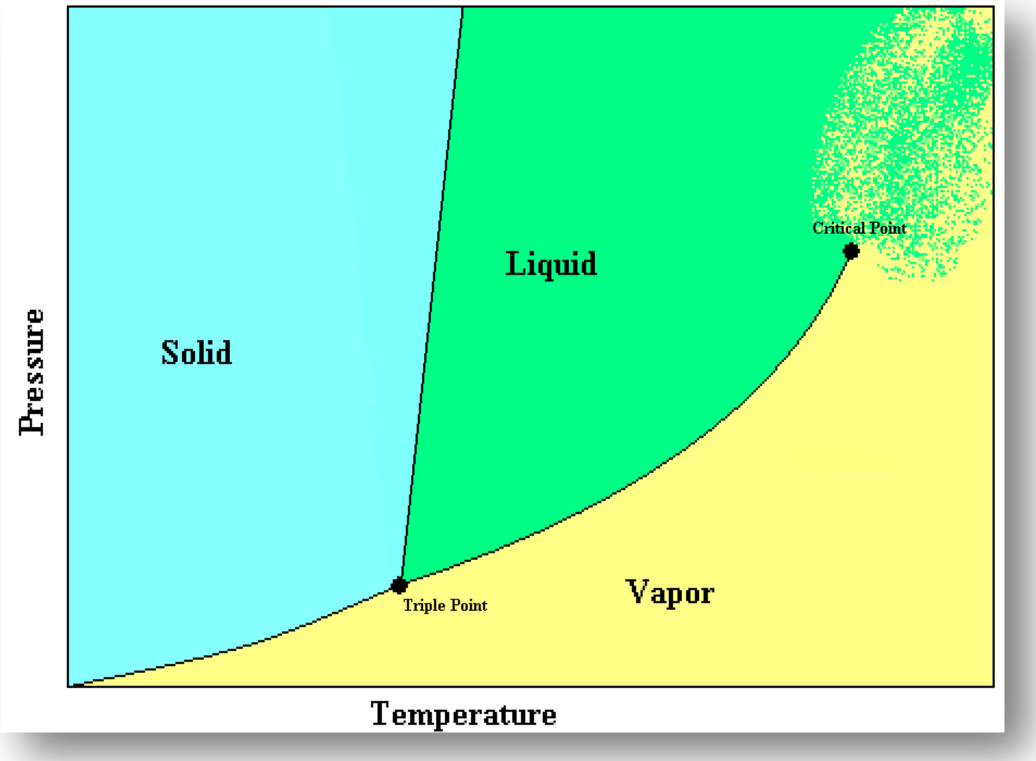


- The lines separating the phases represent points where the two phases can coexist.
- The triple point represents the one and only point on the diagram where all three phases can coexist.

PHASE CHANGE

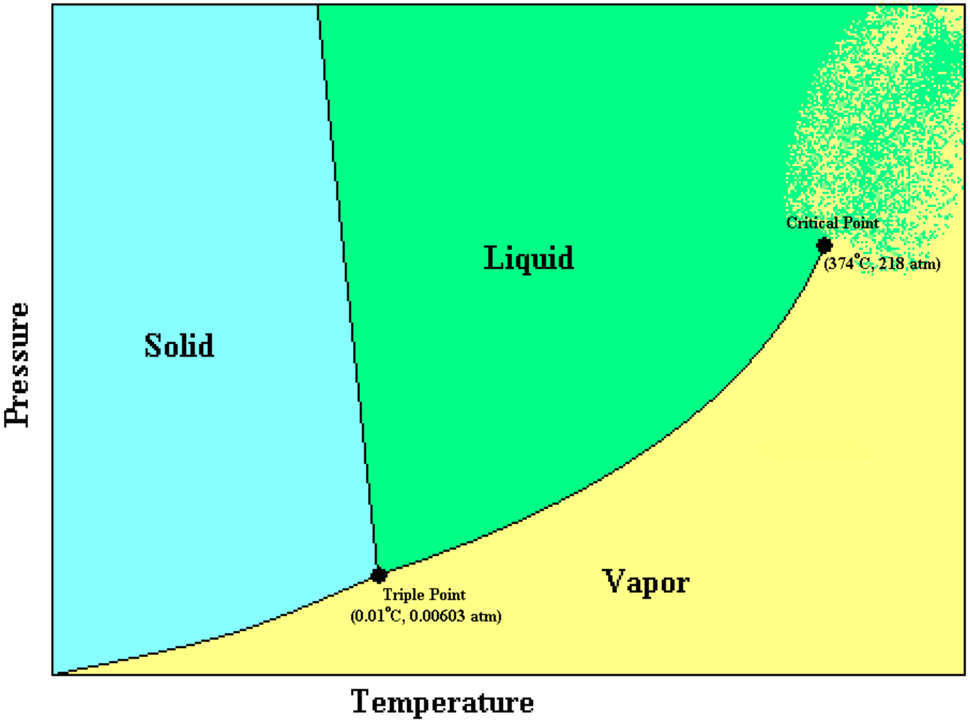
- The critical point occurs at the end of the vapor-to-liquid transition line. At temperatures above the critical temperature, or pressures above the critical pressure there is no distinction between the liquid and vapor phases.

- The slope of the solid-to-liquid transition line shows how the melting point changes with pressure.
- An increase in pressure will increase the melting point.

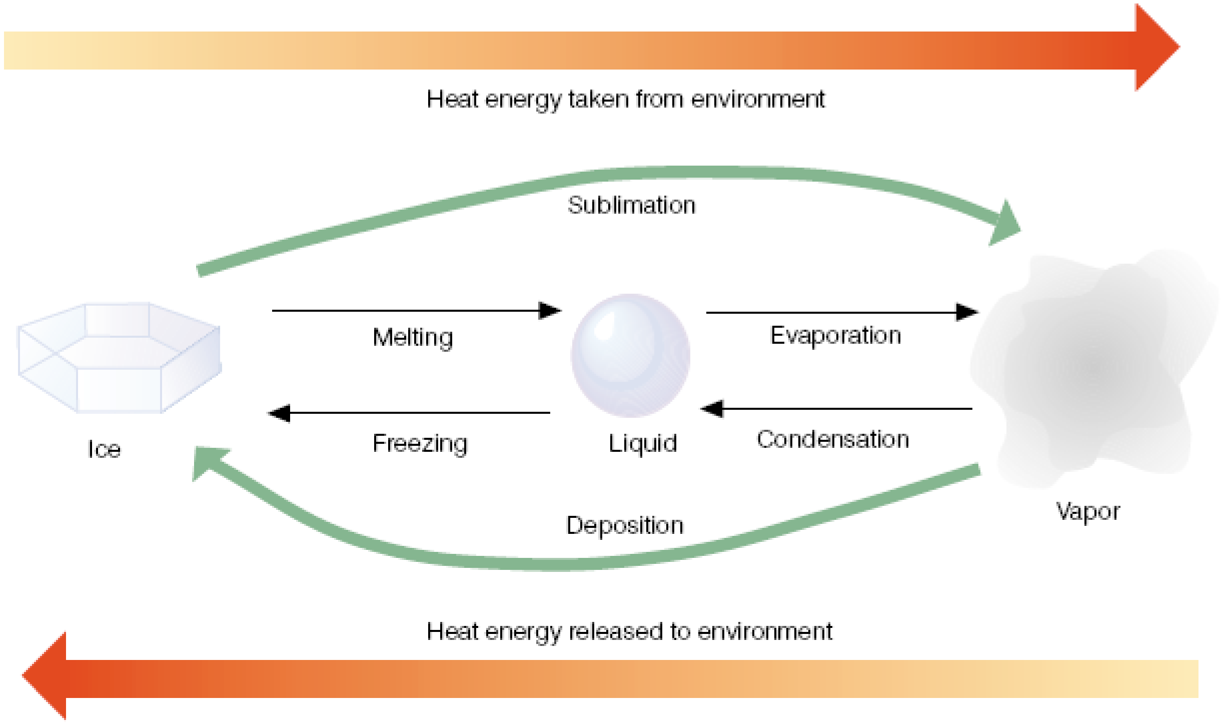


PHASE CHANGE

- Water is one of the few substances that can exist in all three phases at the temperatures and pressures found in the Earth's atmosphere.
- A unique feature of water is that the solid-to-liquid transition line slopes upward to the left, instead of to the right.

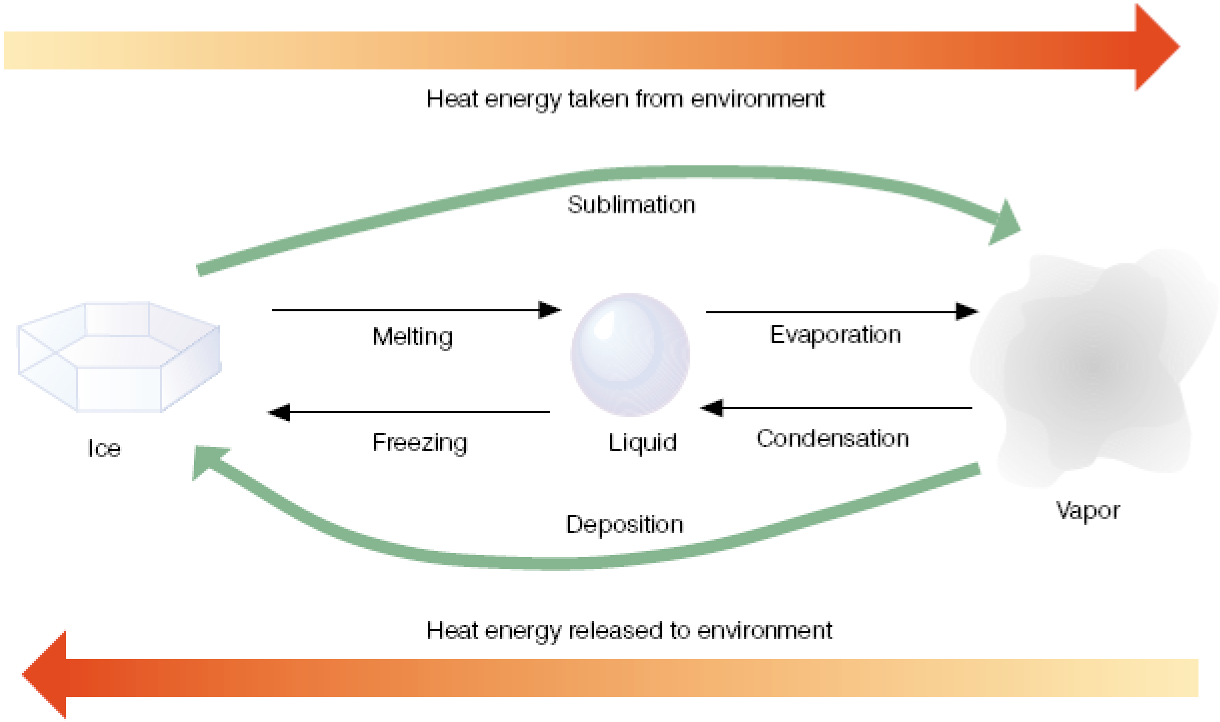


PHASE CHANGE



- When the change of state is from left to right, heat is absorbed by the substance and taken away from the environment.
- The processes of melting, evaporation, and sublimation (ice to vapor) all cool the environment.

PHASE CHANGE



- When the change of state is from right to left, heat energy is given up by the substance and added to the environment.
- The processes of freezing, condensation, and deposition (vapor to ice) all warm their surroundings.

Latent heat is an important source of atmospheric energy, why ??????

Once vapor molecules become separated from the earth’s surface, they are swept away by the wind rising to high altitudes where the air is cold, the vapor changes into liquid and ice cloud particles. During these processes, a huge amount of heat energy is released into the environment. Water vapor evaporated from warm, tropical water can be carried into polar regions, where it condenses and gives up its heat energy.

Thus, evaporation-transportation-condensation is an extremely important mechanism for the relocation of heat energy (as well as water) in the atmosphere.

FYI: A REVIEW OF STATE VARIABLES

- The thermodynamic state of a simple system in thermodynamic equilibrium is completely characterized by specifying the internal energy (U), volume (V), and the number of moles, n_i, of each of its components.
- Example: The thermodynamic state of a one-component, closed system in equilibrium can be completely described by any two state variables (other than mass or moles).
- The state variables have two important properties:
  - The change in any of the state variables (say U) doesn’t depend on the path of the system on a thermodynamic diagram.
  - It only depends on the endpoints.

FYI: A REVIEW OF STATE VARIABLES

Mathematically, this means that differentials of state functions are exact differentials.

$$\int_a^b dU = U(b) - U(a)$$

- **The integral of a state variable around a closed path is zero.**

$$\oint dU = 0$$

Here the problem is going to appear, because HEAT & WORK is not a state variables !!!!!!

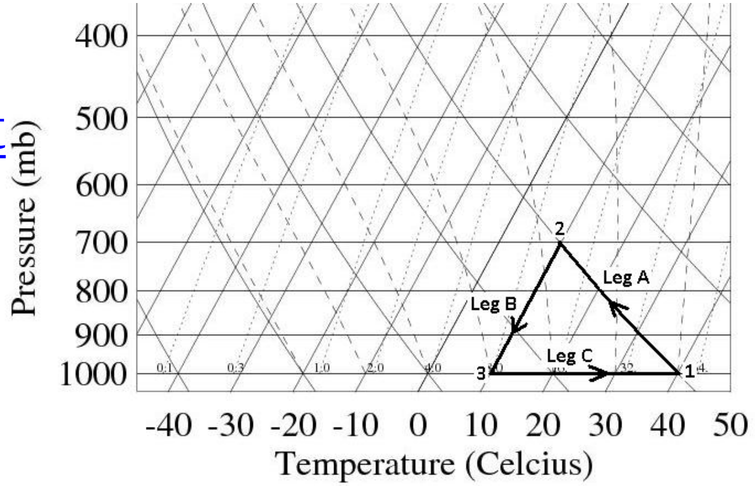
But Heat and work are modes of transfer of energy, thus how can we deal with them to know about the state of thermodynamic System ???

FYI: HEAT IS NOT A STATE VARIABLE

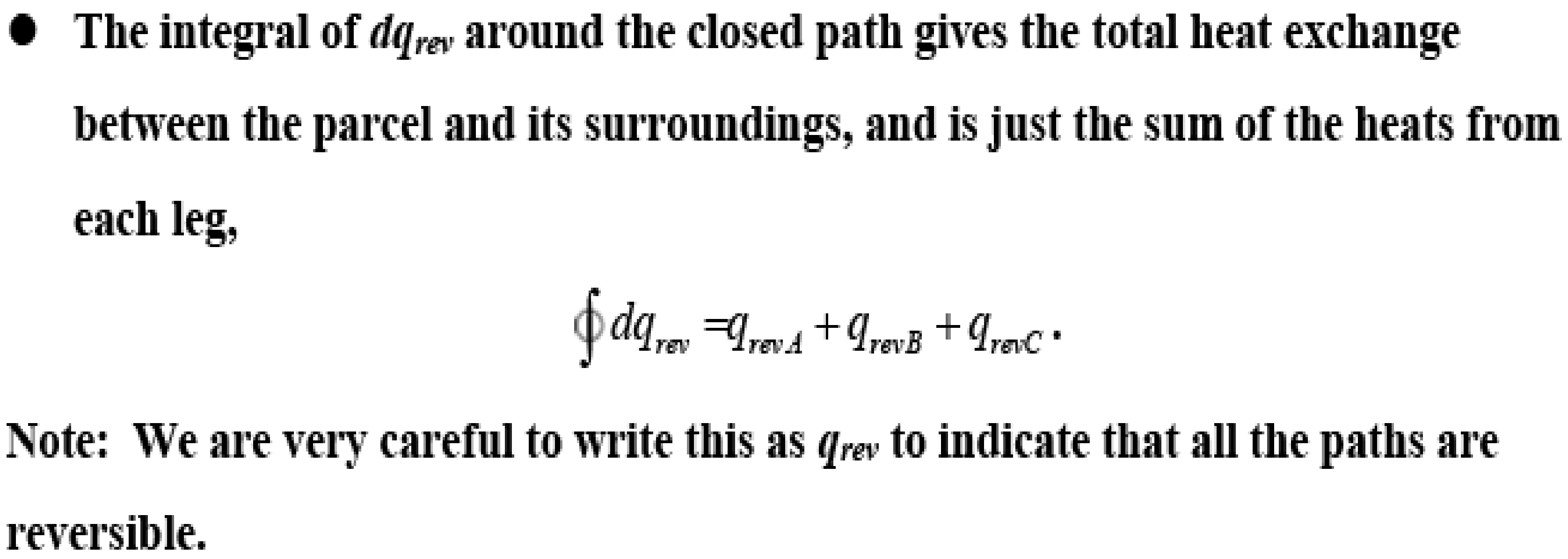
We know why work is not a state variable, but what about heat ????
Imagine that an air parcel starts out at Point 1 on the skew-T diagram shown below. The initial pressure and temperature are p1 and T1. The parcel moves in a reversible, closed cycle around the path shown. The three legs of the path are:

- Leg A: Adiabatic expansion to pressure p2.
- Leg B: Isothermal compression back to pressure p1.
- Leg C: Isobaric heating back to temperature T1.

https://www.weather.gov/jetstream/skewt



FYI: HEAT IS NOT A STATE VARIABLE



- **The integral of dq_{rev} around the closed path gives the total heat exchange between the parcel and its surroundings, and is just the sum of the heats from each leg,**

$$\oint dq_{rev} = q_{revA} + q_{revB} + q_{revC} .$$

Note: We are very careful to write this as q_{rev} to indicate that all the paths are reversible.

FYI: HEAT IS NOT A STATE VARIABLE

- **Leg A is reversibly adiabatic, so**

$$q_{rev\,A} = \int_{\text{Leg A}} dq_{rev} = 0 \tag{1}$$

  - **The temperature at Point 2 is related to the temperature at Point 1 via the Poisson relation**

$$T_2 = T_1 \left(\frac{p_2}{p_1} \right)^{R_d/c_p} . \tag{2}$$

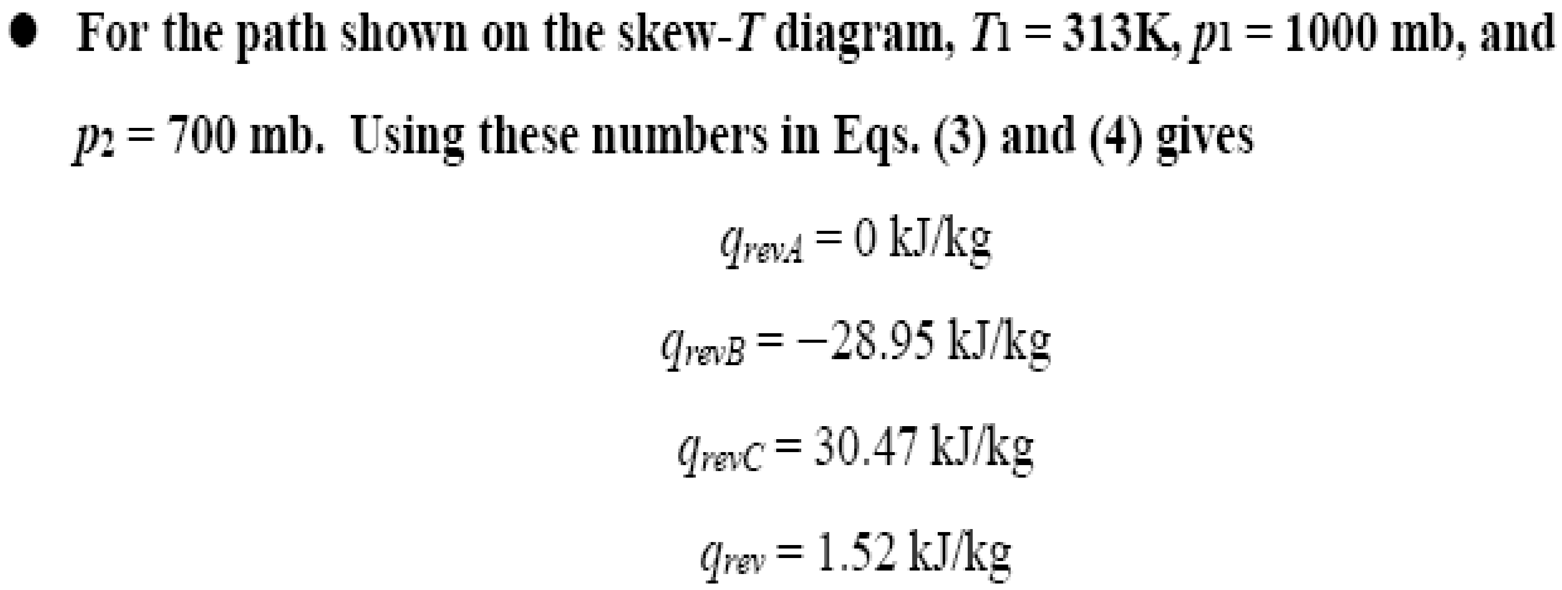
- **Leg B is isothermal. The heat for this leg is therefore**

$$q_{rev\,B} = -R_d T_2 \ln \frac{p_1}{p_2} = -R_d \left[T_1 \left(\frac{p_2}{p_1} \right)^{R_d/c_p} \right] \ln \frac{p_1}{p_2} . \tag{3}$$

- **Leg C is isobaric. The heat along this path is just**

$$q_{rev\,C} = c_p \left(T_1 - T_2 \right) = c_p T_1 \left[1 - \left(\frac{p_2}{p_1} \right)^{R_d/c_p} \right] \tag{4}$$

FYI: HEAT IS NOT A STATE VARIABLE



- For the path shown on the skew-*T* diagram, $T_1 = 313\text{K}$, $p_1 = 1000$ mb, and $p_2 = 700$ mb. Using these numbers in Eqs. (3) and (4) gives

$$q_{revA} = 0 \text{ kJ/kg}$$

$$q_{revB} = -28.95 \text{ kJ/kg}$$

$$q_{revC} = 30.47 \text{ kJ/kg}$$

$$q_{rev} = 1.52 \text{ kJ/kg}$$

Thus, the total heat around the closed, reversible path is not zero. Therefore, heat is not a state variable.

FYI: HEAT IS NOT A STATE VARIABLE

- **The work around the path can be found from the first law of thermodynamics,**

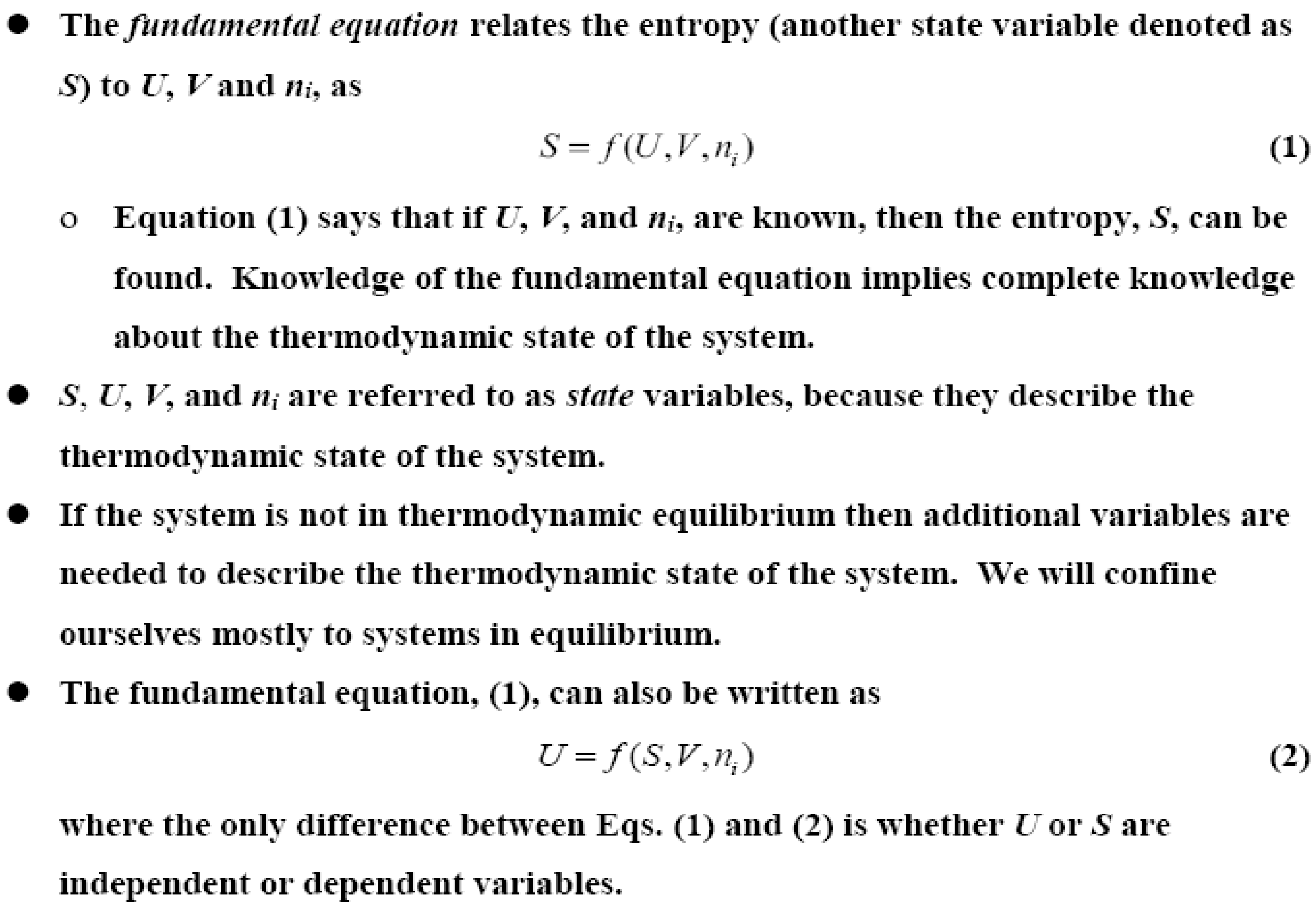
  $$du = dq + dw.$$

  Integrating around the closed path gives

  $$\oint du = \oint dq + \oint dw \;\Rightarrow\; 0 = q + w \;\Rightarrow\; w = -q.$$

- **Since heat and work are not state variables (and are therefore not exact differentials), some texts give their differentials a horizontal slash symbol,** $\text{đ}w$ **and** $\text{đ}q$ **to show this.**

The Fundamental Equation and Entropy



- **The *fundamental equation* relates the entropy (another state variable denoted as *S*) to *U*, *V* and n_i, as**

$$S = f(U, V, n_i) \qquad \textbf{(1)}$$

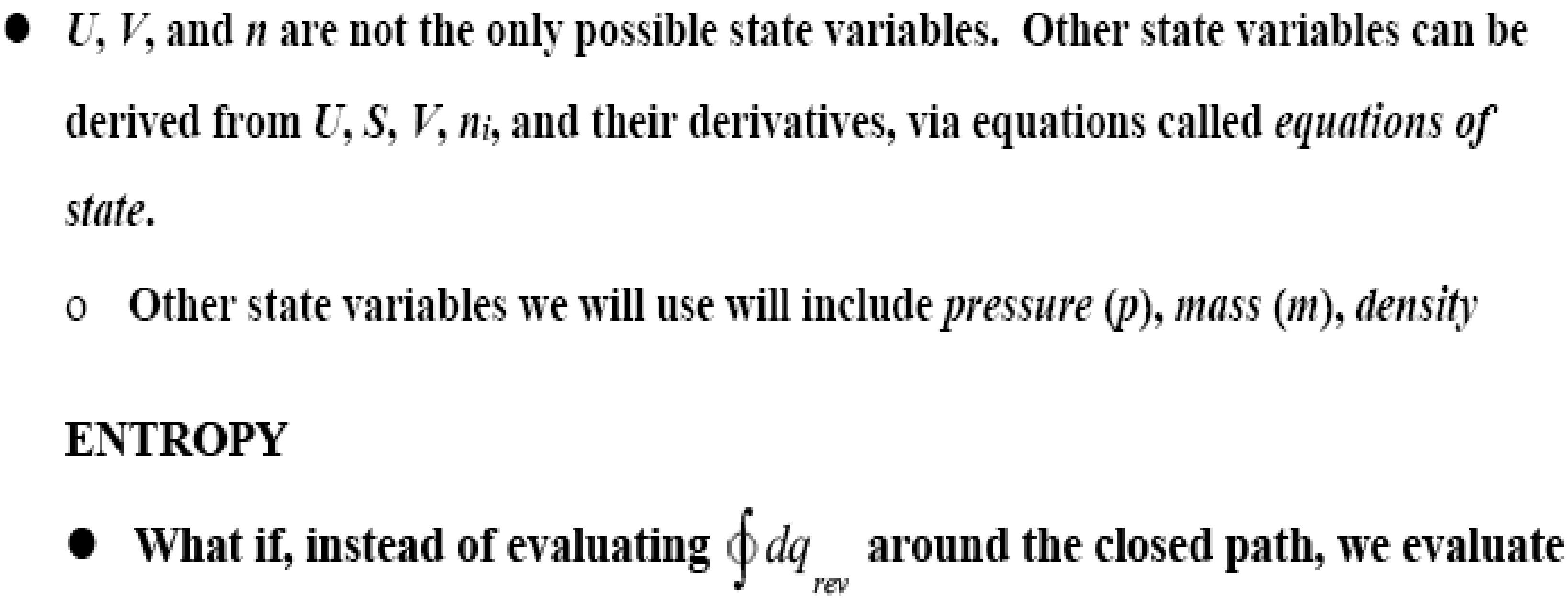
  - **Equation (1) says that if *U*, *V*, and n_i, are known, then the entropy, *S*, can be found. Knowledge of the fundamental equation implies complete knowledge about the thermodynamic state of the system.**

- ***S*, *U*, *V*, and n_i are referred to as *state* variables, because they describe the thermodynamic state of the system.**
- **If the system is not in thermodynamic equilibrium then additional variables are needed to describe the thermodynamic state of the system. We will confine ourselves mostly to systems in equilibrium.**
- **The fundamental equation, (1), can also be written as**

$$U = f(S, V, n_i) \qquad \textbf{(2)}$$

where the only difference between Eqs. (1) and (2) is whether *U* or *S* are independent or dependent variables.

The Fundamental Equation and Entropy



- *U*, *V*, and *n* are not the only possible state variables. Other state variables can be derived from *U*, *S*, *V*, n_i, and their derivatives, via equations called *equations of state*.
  - Other state variables we will use will include *pressure* (*p*), *mass* (*m*), *density*

ENTROPY

- What if, instead of evaluating $\oint dq_{rev}$ around the closed path, we evaluate

PAY ATTENTION WHY WE DIVIDED BY T ???

FYI: The Fundamental Equation and Entropy

- **For Leg A, dq_{rev} was zero, so the integral is still zero**

$$\int_{\text{Leg A}} \frac{dq_{rev}}{T} = 0 \qquad \textbf{(5)}$$

- **For Leg B (the isothermal leg)**

$$\int_{\text{Leg B}} \frac{dq_{rev}}{T} = -\int_{\text{Leg B}} \frac{\alpha dp}{T} = -R_d \int_{\text{Leg B}} \frac{dp}{p} = -R_d \ln \frac{p_1}{p_2}\,. \qquad \textbf{(6)}$$

- **For Leg C (the isobaric leg)**

$$\int_{\text{Leg C}} \frac{dq_{rev}}{T} = \int_{\text{Leg C}} \frac{c_p dT}{T} = c_p \int_{\text{Leg C}} \frac{dT}{T} = c_p \ln \frac{T_1}{T_2}\,.$$

But, from Eq. (2), we have

$$\frac{T_1}{T_2} = \left(\frac{p_1}{p_2}\right)^{R_d/c_p},$$

so

$$\int_{\text{Leg C}} \frac{dq_{rev}}{T} = c_p \ln\left(\frac{p_1}{p_2}\right)^{R_d/c_p} = R_d \ln \frac{p_1}{p_2}\,. \qquad \textbf{(7)}$$

Entropy

- **Summing the results for the three legs [Eqs. (5), (6), and (7)] we have**

$$\oint \frac{dq_{rev}}{T} = \int_{\text{Leg A}} \frac{dq_{rev}}{T} + \int_{\text{Leg B}} \frac{dq_{rev}}{T} + \int_{\text{Leg C}} \frac{dq_{rev}}{T} = R_d \ln \frac{p_1}{p_2} - R_d \ln \frac{p_1}{p_2} ,$$

$$\oint \frac{dq_{rev}}{T} = 0 \qquad \textbf{(8)}$$

- **Eq. (8) implies that dq_{rev}/T is an exact differential, and therefore, must be the differential of a state variable.**

$$\oint ds = \oint \frac{dq_{rev}}{T} \qquad \textbf{(9)}$$

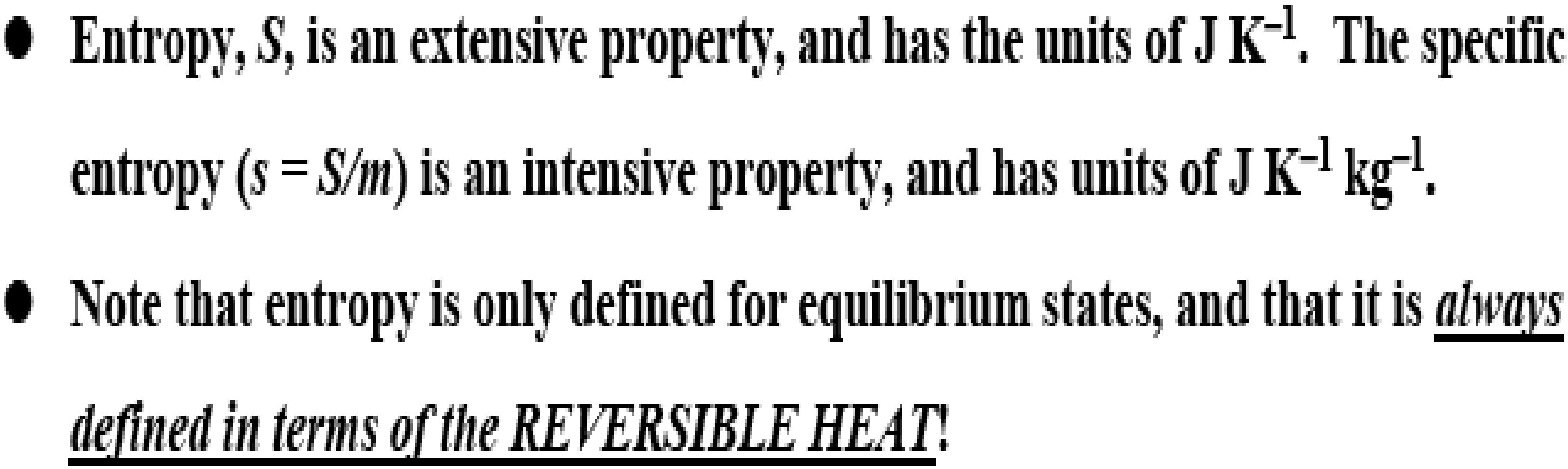
- **We call this state variable the specific entropy, and denote it by s. Therefore,**

$$ds \equiv \frac{dq_{rev}}{T} . \qquad \textbf{(10)}$$

- **Multiplying Eq. (10) by mass, we get an extensive quantity called entropy,**

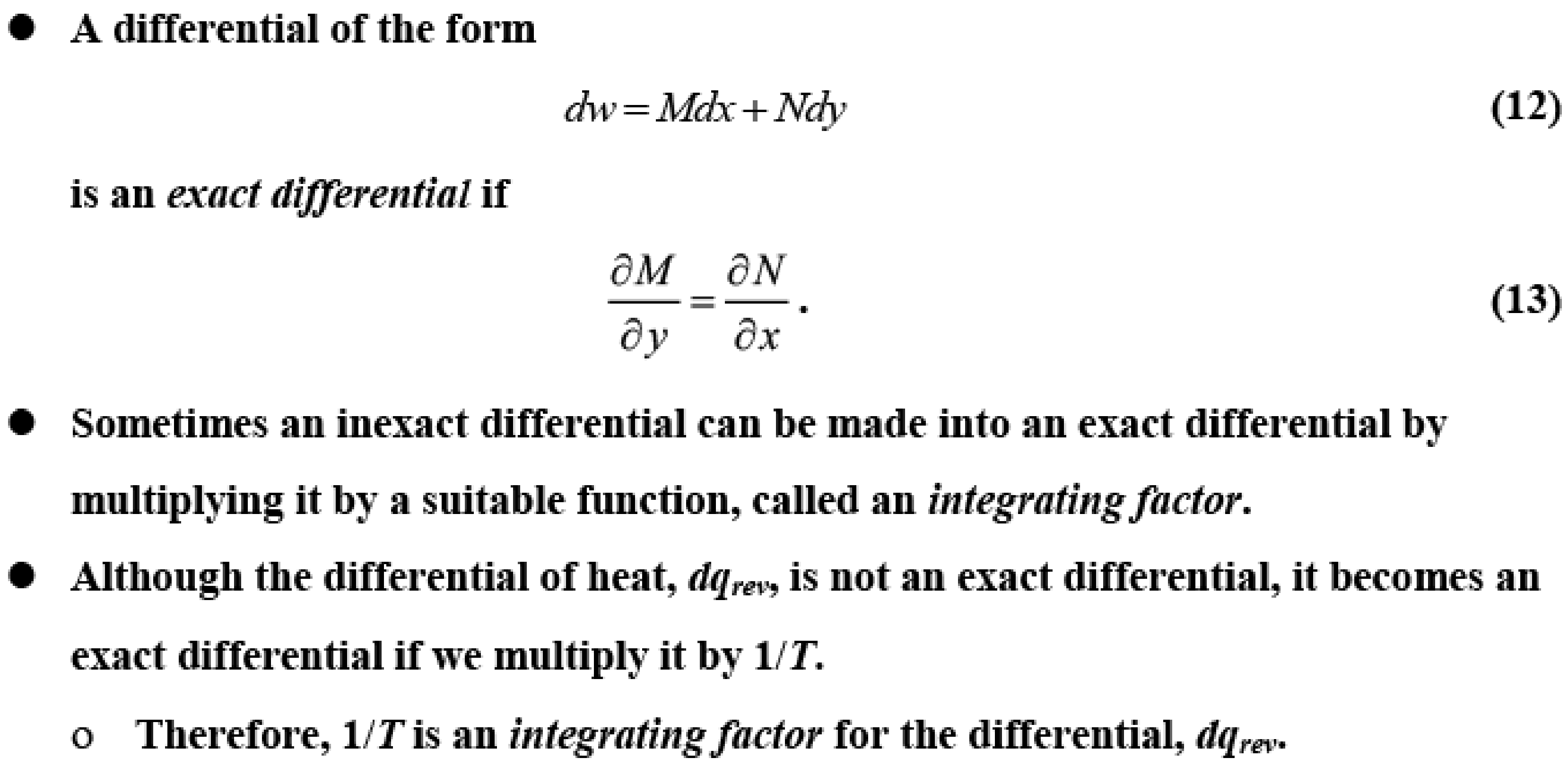
$$dS \equiv \frac{dQ_{rev}}{T} . \qquad \textbf{(11)}$$

Entropy



- Entropy, S, is an extensive property, and has the units of J K^{-1}. The specific entropy ($s = S/m$) is an intensive property, and has units of J K^{-1} kg^{-1}.
- Note that entropy is only defined for equilibrium states, and that it is *always defined in terms of the REVERSIBLE HEAT*!

Why we divided the HEAT Q by T ?



- **A differential of the form**

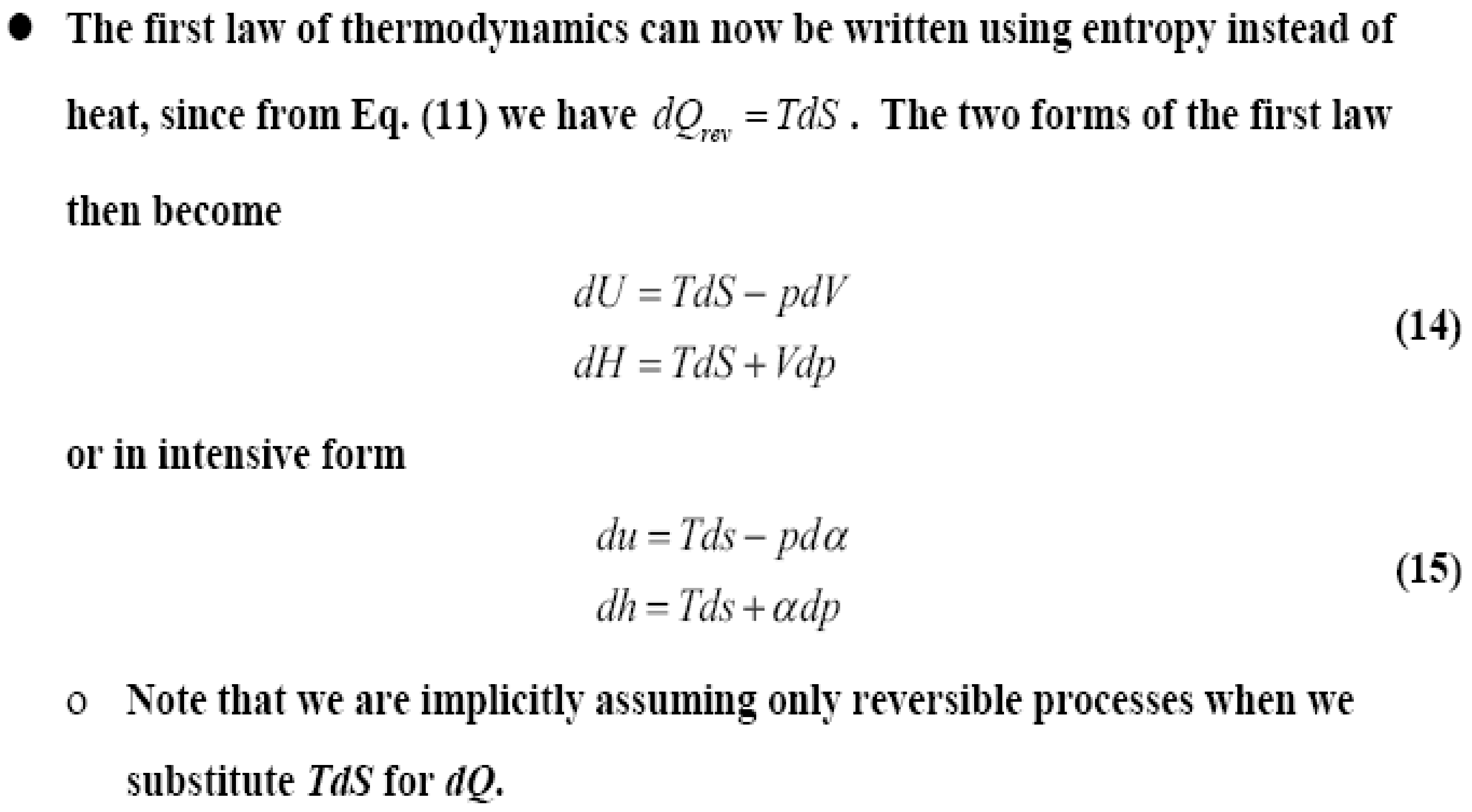
$$dw = Mdx + Ndy \qquad \textbf{(12)}$$

is an *exact differential* if

$$\frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}\,. \qquad \textbf{(13)}$$

- **Sometimes an inexact differential can be made into an exact differential by multiplying it by a suitable function, called an *integrating factor*.**
- **Although the differential of heat, dq_{rev}, is not an exact differential, it becomes an exact differential if we multiply it by $1/T$.**
  - **Therefore, $1/T$ is an *integrating factor* for the differential, dq_{rev}.**

What are the thermodynamic definition of temperature & pressure using Entropy and 1st law of thermodynamics???



- The first law of thermodynamics can now be written using entropy instead of heat, since from Eq. (11) we have $dQ_{rev} = TdS$. The two forms of the first law then become

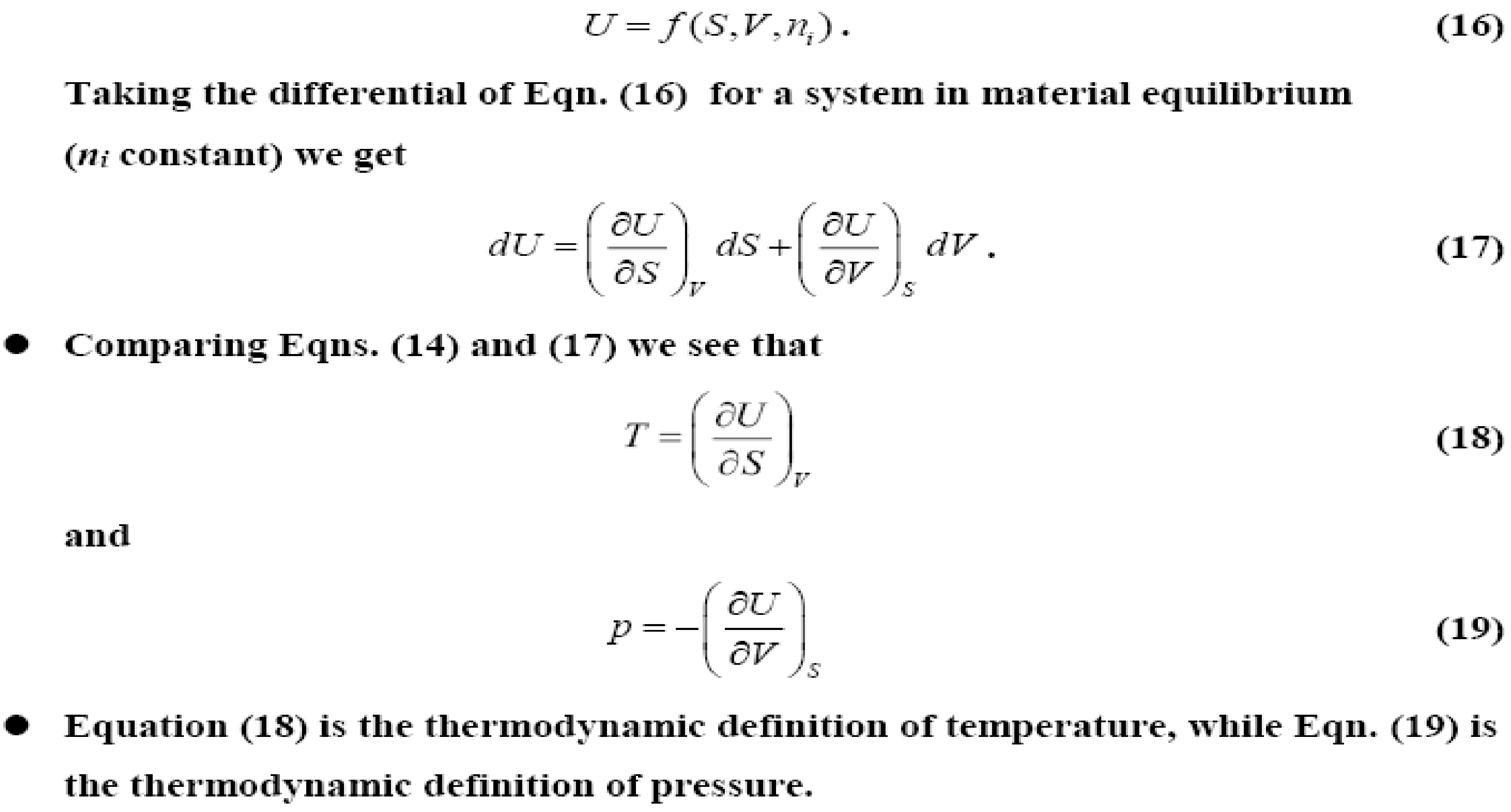
$$dU = TdS - pdV$$
$$dH = TdS + Vdp \quad (14)$$

or in intensive form

$$du = Tds - pd\alpha$$
$$dh = Tds + \alpha dp \quad (15)$$

  - Note that we are implicitly assuming only reversible processes when we substitute ***TdS*** for ***dQ***.

What are the thermodynamic definition of temperature & pressure using Entropy and 1st law of thermodynamics???



$$U = f(S, V, n_i)\,. \qquad (16)$$

Taking the differential of Eqn. (16) for a system in material equilibrium (n_i constant) we get

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV\,. \qquad (17)$$

- **Comparing Eqns. (14) and (17) we see that**

$$T = \left(\frac{\partial U}{\partial S}\right)_V \qquad (18)$$

and

$$p = -\left(\frac{\partial U}{\partial V}\right)_S \qquad (19)$$

- **Equation (18) is the thermodynamic definition of temperature, while Eqn. (19) is the thermodynamic definition of pressure.**