

# CLAUSIUS INEQUALITY AND ENTROPY

– with a little history thrown in.

**CARNOT** PROPOSED THAT HEAT MUST ALWAYS BE WASTED IN ORDER FOR A HEAT ENGINE TO PRODUCE NET WORK, BUT HE DID NOT QUANTIFY HOW MUCH HEAT HAD TO BE WASTED.

IN ~ 1850 **RUDOLF CLAUSIUS** CONFIRMED THE EXISTING THEORIES:

1. ENERGY IS CONSERVED (1<sup>ST</sup> LAW) WAS QUANTIFIED AS  
 $Q - W = \Delta U$
2. HEAT FLOWS NATURALLY FROM HOT TO COLD (NOT QUANTIFIED)

AND ADDED AN IMPORTANT CONTRIBUTION:

CLAUSIUS KNEW THAT SOME HEAT HAD TO BE REJECTED FROM A REVERSIBLE (CARNOT) HEAT ENGINE ( $Q_L$ ), AS CARNOT PROPOSED, AND HE KNEW THAT

$$Q_L = W_{\text{net}} - Q_H \quad (1^{\text{ST}} \text{ LAW})$$

BUT NO PRINCIPLE FIXED THE ABSOLUTE AMOUNT OF REJECTED HEAT.

CLAUSIUS THEN OBSERVED THAT FOR REVERSIBLE HEAT ENGINES, THE RATIO OF THE HEAT INPUT TO THE REJECTED HEAT WAS CONSISTENTLY EQUAL TO THE RATIO OF THE ABSOLUTE TEMPERATURES OF THE HIGH AND LOW TEMPERATURE RESERVOIRS:

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L} \quad (1)$$

If and only if the temperature of the high ( $T_H$ ) and low ( $T_L$ ) temperature reservoirs are always expressed in degrees Kelvin.

REARRANGING (1) FOR A REVERSIBLE HEAT ENGINE:

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L} \quad (2)$$

CLAUSIUS THEN EXAMINED IRREVERSIBLE PROCESSES AND FOUND THAT THE RELATION (2) DID NOT HOLD. HE REASONED, FOR EXAMPLE, IF 10 JOULES OF HEAT FLOW FROM A HOT OBJECT AT 350K INTO A COOL ROOM AT 300K, THEN THE HEAT TRANSFER TERM FOR HEAT LEAVING THE OBJECT AND HEAT TRANSFERRED INTO THE ROOM IS THE SAME AND

$$\frac{Q}{T_H} < \frac{Q}{T_L} \text{ or } \frac{10}{350} < \frac{10}{300} \quad (3)$$

That is, for irreversible processes, the ratio of heat over absolute temperature increases in the direction of natural heat flow.

COMBINING (2) AND (3) FOR A HEAT ENGINE WITH ONE HEAT INPUT AND ONE HEAT OUTPUT:

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} \leq 0 \quad (4)$$

OR FOR ANY SEQUENCE OF PROCESSES WITH DISCRETE HEAT TRANSFER TERMS:

$$\sum_{\text{K}} \left( \frac{Q}{T} \right)_{\text{K}} \leq 0 \quad (5)$$

WHERE  $\left( \frac{Q}{T} \right)_{\text{K}}$  = THE RATIO OF THE AMOUNT OF HEAT TRANSFERRED IN A PROCESS TO THE TEMPERATURE OF THE SURROUNDINGS WHERE HEAT IS TRANSFERRED

CALCULATING THE RATIO AS THE INTEGRAL OF A CONTINUOUS FUNCTION OF  $\frac{\delta Q}{T}$ , CLAUSIUS' PRINCIPLE FOR A REVERSIBLE OR IRREVERSIBLE CYCLE IS:

$$\oint \left( \frac{\delta Q}{T} \right) \leq 0 \quad (6)$$

**FOR REVERSIBLE CYCLES:**

$$\oint \left( \frac{\delta Q}{T} \right) = 0 \quad \text{and} \quad \sum_{\text{K}} \left( \frac{Q}{T} \right)_{\text{K}} = 0 \quad (7)$$

**FOR IRREVERSIBLE CYCLES:**

$$\oint \left( \frac{\delta Q}{T} \right) < 0 \quad \text{and} \quad \sum_{\text{K}} \left( \frac{Q}{T} \right)_{\text{K}} < 0 \quad (8)$$

The ratio of heat to temperature has characteristics of a property, since it does not change in a cycle, but it is also associated with heat transfer (a path function). In a paper published in 1865, “*On various forms of the laws of thermodynamics that are convenient for applications,*” Clausius named the heat:temperature ratio **entropy**, from the Greek word for “transformation” with the symbol for entropy, the letter “**S**.” Clausius’ 1865 paper ends with a bold statement that is the broadest possible application of the laws of thermodynamics:

- 1. The energy of the universe is constant (1<sup>st</sup> Law)**
- 2. The entropy of the universe tends toward a maximum (2<sup>nd</sup> Law)**

Clausius’ statement of the 2<sup>nd</sup> Law of Thermodynamics and his discovery of entropy as the ratio of two macroscopic components: heat and absolute temperature, was truly remarkable since the true nature of entropy was only discovered later when physicists understood the nature of individual atoms and molecules – the microscopic world.

It was the physicist **Ludwig Boltzmann** who in 1905 proposed that the nature of entropy is related to the probability of the state of the atoms or molecules in a system. That is, if the order or arrangement of molecules is unique – has a low probability – then the entropy is low. In contrast, there are many possible combinations of arrangements to obtain a disorderly system – with a high probability – then the entropy is high. For example, if a deck of cards were arranged with the four suits separated and ordered ♣-♦-♥-♠ and all the cards in each suit in ascending sequence (A-K), the arrangement is unique, the probability of accidentally achieving such an arrangement is very low, and the entropy is very low. However, for disorderly arrangements of the cards (suits not in order, cards not in sequence), there are an increasing number of ways to achieve increasingly random arrangements and the entropy increases correspondingly. **Boltzmann's complete explanation of entropy:**

- 1. Qualitatively, entropy is disorder, which has a natural tendency to increase.**
- 2. Entropy is measured by the ratio of heat to absolute temperature.**
- 3. Entropy is theoretically related to the size (number of digits) in the probability space for the arrangement of atoms/molecules in a system.**

**It follows from Boltzmann's contribution, that the entropy of a pure crystalline substance at  $T = 0$  K (absolute zero) is zero – no random arrangement. (Sometimes called the 3<sup>rd</sup> Law of Thermodynamics.)**

From Clausius' principle, for an INTERNALLY REVERSIBLE PROCESS, ENTROPY IN A CLOSED SYSTEM IS:

$$dS = \frac{\delta Q}{T}$$

$$\int_1^2 dS = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} \quad \text{for reversible processes (9)}$$

for an IRREVERSIBLE PROCESS, ENTROPY IN A CLOSED SYSTEM IS:

$$dS > \frac{\delta Q}{T}$$

$$\int_1^2 dS = S_2 - S_1 > \int_1^2 \frac{\delta Q}{T}$$

defining  $S_{\text{gen}}$  as the entropy generated in the surroundings, as the

difference:  $\left(\frac{\delta Q}{T}\right)_{\text{irreversible}} - \left(\frac{\delta Q}{T}\right)_{\text{reversible}}$  so  $S_{\text{gen}} > 0$  for irreversible

**processes:**

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{\text{gen}} \quad \text{for irreversible processes (10)}$$

Special cases for equation (10):

**1. Reversible processes**

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T}$$

**2. Adiabatic processes**

$$S_2 - S_1 = S_{\text{gen}}$$

**3. Reversible AND Adiabatic processes are ISENTROPIC.**

$$S_2 - S_1 = 0$$

**ENTROPY IN OPEN SYSTEMS (CONTROL VOLUME)**

$$\frac{dS_{\text{cv}}}{dt} = \sum_k \left( \frac{\dot{Q}}{T} \right)_k + \sum_i \dot{m}_i s_i - \sum_e \dot{m}_e s_e + \dot{S}_{\text{gen}}$$

In steady-state conditions,  $\frac{dS_{\text{cv}}}{dt} = 0$  and

$$\sum_e \dot{m}_e s_e - \sum_i \dot{m}_i s_i = \sum_k \left( \frac{\dot{Q}}{T} \right)_k + \dot{S}_{\text{gen}} \quad (11)$$

Special Cases for equation (11) for control volumes (open systems):

1. For an **open system with a single inlet and outlet at steady-state**:

$$\dot{m}(s_e - s_i) = \sum_k \left( \frac{\dot{Q}}{T} \right)_k + \dot{S}_{\text{gen}}$$

2. For an **adiabatic process in an open system at steady-state with single inlet and outlet**:

$$\dot{m}(s_e - s_i) = \dot{S}_{\text{gen}}$$

3. for a **reversible process in an open system at steady-state with single inlet and outlet**:

$$\dot{m}(s_e - s_i) = \sum_k \left( \frac{\dot{Q}}{T} \right)_k$$

4. for **an adiabatic and reversible process in an open system at steady-state (isentropic process)**

$$s_e - s_i = 0$$

**ENTROPY FOR A CYCLE:  $\Delta S = 0$  and**

$$\dot{S}_{\text{gen}} = -\sum_k \left( \frac{\dot{Q}}{T} \right)_k$$



## UNITS OF ENTROPY:

intensive property,  $s$ :  $\frac{\text{kJ}}{\text{kg} - \text{K}}$

extensive property,  $S$ :  $\frac{\text{kJ}}{\text{K}}$

rate of entropy change/transfer:  $\dot{m}s = \dot{S} : \frac{\text{kw}}{\text{K}}$

**SIGN CONVENTION FOR S IS THE SAME AS FOR HEAT.**

**IF HEAT IS TRANSFERRED INTO THE SYSTEM ( $Q > 0$ ) THEN THE ENTROPY OF THE SYSTEM INCREASES ( $\Delta S > 0$ ).**

**IF HEAT IS TRANSFERRED OUT OF THE SYSTEM ( $Q < 0$ ) THEN THE ENTROPY OF THE SYSTEM MUST DECREASE ( $\Delta S < 0$ ).**

Results of entropy:

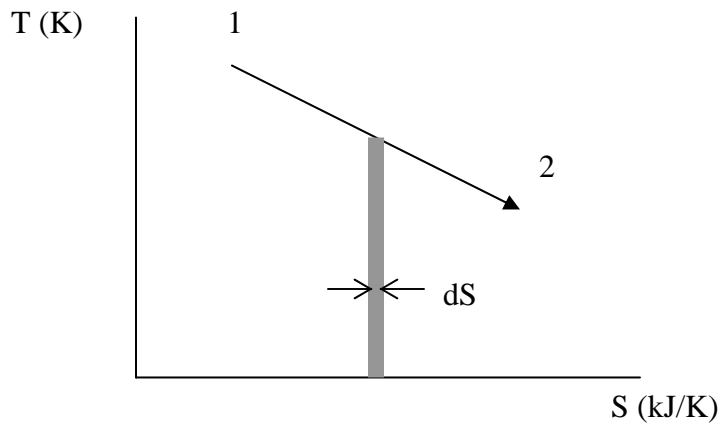
- A. Equilibrium can be defined as a state of maximum entropy of an isolated system, and spontaneous changes only occur in the direction of increasing entropy of the universe ( $S_{\text{gen}}$ ).
- B. Entropy is NOT conserved in real (irreversible processes).
- C. The magnitude of generated entropy is proportional to the magnitudes of irreversibilities.

## THE TEMPERATURE-ENTROPY, T-S, DIAGRAM

Clausius' principle for an internally reversible process:

$$\delta Q = TdS$$

Any process can be graphed on a T-S (or T-s) diagram (just as with T-v or P-v diagrams). Because of Clausius' Principle, the T-S diagrams for internally reversible processes can be used to calculate heat transfer.

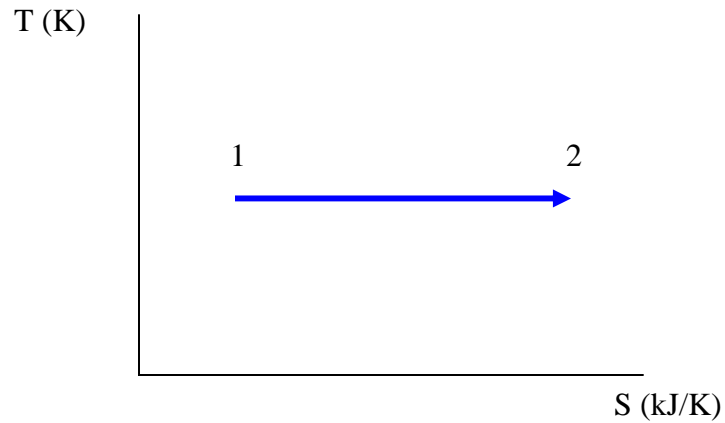


Shaded area =  $TdS = \delta Q$  and the total area under process line for the internally reversible process  $1 \rightarrow 2$  is the heat transferred during the process:

$$\int_1^2 TdS = Q_{1 \rightarrow 2}$$

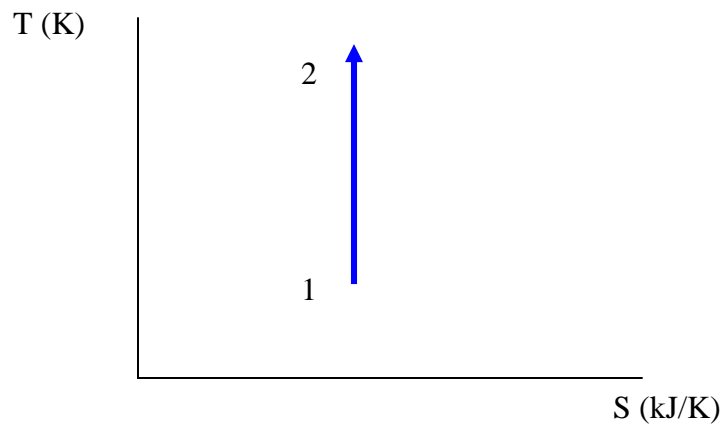
## SPECIAL T-S DIAGRAMS

1. For an isothermal internally reversible process:



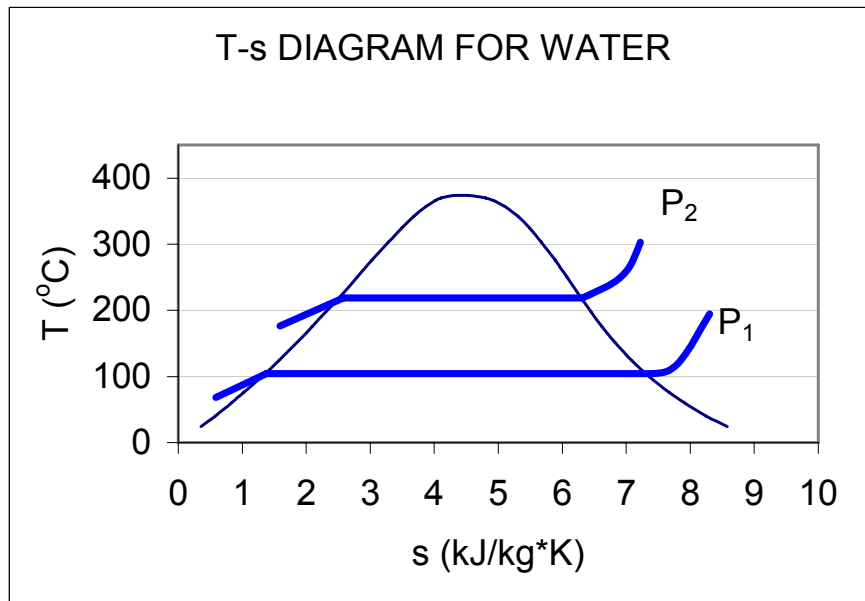
$$Q_{1 \rightarrow 2} = T(S_2 - S_1) =$$

2. For an adiabatic and internally reversible process (isentropic):



$$(S_2 - S_1) = 0$$

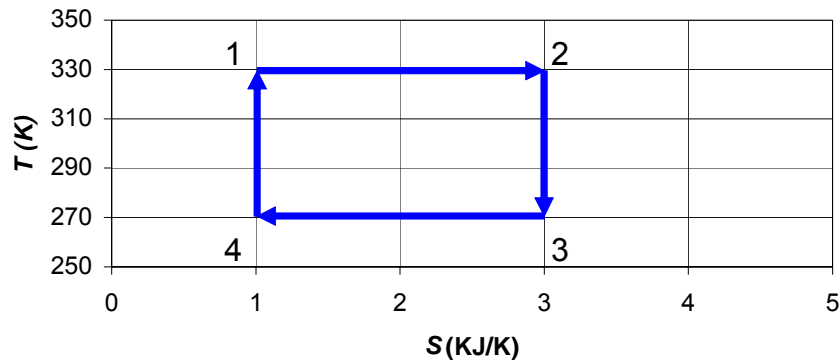
3. For pure substances with liquid vapor phases, the T-s diagram shows similar constant pressure lines as in the P-v and T-v diagrams, indicating vaporization/condensation processes at constant pressure are isothermal and as P increases,  $s_{fg}$  decreases:



where  $P_2 > P_1$ . As with the T-s and P-v diagrams, the critical point (where liquid and vapor phases are indistinguishable) is at the top of the phase curve where the saturated liquid and vapor lines meet. A pure substance is compressed liquid for  $s < s_f$ , superheated vapor for  $s > s_g$ , and a saturated liquid-vapor mixture between the saturated liquid and vapor lines.

#### 4. For Carnot cycles:

##### (a) Carnot Heat Engine – all totally reversible processes



1→2 is isothermal expansion, the heat input process, and  $Q_H =$  area under line 1-2 or  $Q_H = T_1(s_2-s_1)$  (will be positive)

2→3 is isentropic (adiabatic and reversible) expansion, the work output process.  $W_{2\rightarrow3}$  cannot be inferred from the T-S diagram.

3→4 is isothermal compression, the heat rejection process, and  $Q_L =$  area under line 3-4 or  $Q_L = T_3(s_4-s_3)$  (will be negative and  $<Q_H$ )

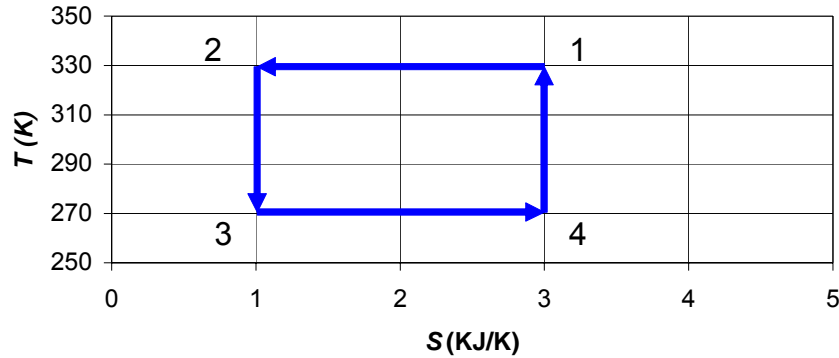
4→1 is isentropic (adiabatic and reversible) compression, the work input process.  $W_{4\rightarrow1}$  cannot be inferred from the T-S diagram.

For the Carnot heat engine cycle, net heat transfer,  $Q_{net}$ , is the area 1-2-3-4 or  $Q_{net} = (T_1-T_4)(s_2-s_1)$  (will be positive), and by the 1<sup>st</sup> Law for cycles:  $Q_{net} = W_{net}$

By Clausius' principle, the entropy generated in a Carnot heat engine cycle is zero, which can be shown using the T-S diagram above and noting that  $\Delta S = 0$  for a cycle:

$$S_{gen} = -\sum_k \left( \frac{Q}{T} \right)_k = -\frac{330(2)}{330} - \left( \frac{-270(2)}{270} \right) = 0$$

**(b) Carnot Refrigerator – all totally reversible processes**



1→2 is isothermal compression, the heat rejection process, and  $Q_H =$  area under line 1-2 or  $Q_H = T_1(s_2-s_1)$  (will be negative)

2→3 is isentropic (adiabatic and reversible) compression, the work input process.  $W_{2\rightarrow3}$  cannot be inferred from the T-S diagram.

3→4 is isothermal expansion, the heat input process, and  $Q_L =$  area under line 3-4 or  $Q_L = T_3(s_4-s_3)$  (will be positive and  $< Q_H$ )

4→1 is isentropic (adiabatic and reversible) expansion, the work output process.  $W_{4\rightarrow1}$  cannot be inferred from the T-S diagram.

For the Carnot refrigeration cycle, net heat transfer,  $Q_{net}$ , is the area 1-2-3-4 or  $Q_{net} = (T_1-T_4)(s_2-s_1)$  (will be negative), and by the 1<sup>st</sup> Law for cycles:  $Q_{net} = W_{net}$

By Clausius' principle, the entropy generated in a Carnot refrigeration cycle is zero, which can be shown using the T-S diagram above and noting that  $\Delta S = 0$  for a cycle:

$$S_{gen} = -\sum_k \left( \frac{Q}{T} \right)_k = -\left( \frac{-330(2)}{330} \right) - \left( \frac{270(2)}{270} \right) = 0$$

# CALCULATING ENTROPY CHANGE, $\Delta S$

Objective: express the entropy of a system as a function of measurable intensive properties (like what we did for the energy of a system, (u and h). For the derivation below, assume internally reversible processes.

1<sup>st</sup> Law:

$$\delta Q - \delta W = dU \quad (1)$$

Clausius' Principle:

$$\delta Q = TdS \quad (2)$$

Definition:

$$\delta W = PdV \quad (3)$$

Substituting (2) and (3) into (1):

$$TdS = dU + PdV \quad (4 - \text{extensive properties})$$

or

$$\mathbf{Tds = du + Pdv} \quad \mathbf{(4a - intensive properties)}$$

Note that the formulas 4 and 4a do not depend on process path (all terms are properties) so they are true for BOTH reversible and irreversible processes.

Also, since  $h = u + Pv$  and  $dh = du + vdP + Pdv$ , or  $du = dh - Pdv - vdP$ .

Substituting for du in (4a):

$$TdS = dh - Pdv - vdP + Pdv$$

$$\mathbf{Tds = dh - vdP} \quad \mathbf{(5)}$$

$$ds = \frac{du}{T} + \frac{Pdv}{T} \quad (6)$$

Dividing 4a and 5 through by T:

$$ds = \frac{dh}{T} - \frac{vdP}{T} \quad (7)$$

(6) and (7) show that if you know the terms on the right hand side, you can find the entropy change in a process. They are equivalent formulas and may be used interchangeably depending on the problem conditions.

## Cases

### 1. IDEAL LIQUID & SOLIDS ARE INCOMPRESSIBLE: $dv = 0$

From (6):

$$ds = \frac{du}{T}$$

also specific heat

$$C_v = \frac{du}{dT}$$

so

$$ds = \frac{C_v dT}{T}$$

and

$$\int_1^2 ds = \int_1^2 \frac{C_v dT}{T}$$

for  $C_v$  constant:

$$s_2 - s_1 = C_v \ln\left(\frac{T_2}{T_1}\right) \quad (8)$$

where T is absolute temperature (K) and  $C_v$  is the average specific heat.

**FOR IDEAL LIQUIDS AND SOLIDS, ISOTHERMAL PROCESSES ARE ISENTROPIC.**



## 2. IDEAL GASES

(a)

FOR AN IDEAL GAS: 
$$P = \frac{RT}{v}$$

Substituting  $C_v dT$  for  $du$  and  $RT/v$  for  $P$  in (6):

$$ds = \frac{C_v dT}{T} + \frac{RTdv}{vT}$$
$$ds = \frac{C_v dT}{T} + \frac{Rdv}{v}$$

integrating both sides with  $C_v$  constant:

$$s_2 - s_1 = C_v \ln\left(\frac{T_2}{T_1}\right) + R \ln\left(\frac{v_2}{v_1}\right) \quad (9)$$

(b) similarly

FOR AN IDEAL GAS: 
$$v = \frac{RT}{P}$$

Substituting  $C_p dT$  for  $dh$  and  $RT/P$  for  $v$  in (7):

$$ds = \frac{C_p dT}{T} - \frac{RTdP}{PT}$$
$$ds = \frac{C_p dT}{T} - \frac{RdP}{P}$$

integrating both sides with  $C_p$  constant:

$$s_2 - s_1 = C_p \ln\left(\frac{T_2}{T_1}\right) - R \ln\left(\frac{P_2}{P_1}\right) \quad (10)$$

where T is always absolute temperature (K).

(9) and (10) are equivalent formulas and either may be used for ideal gas entropy change calculations, depending on which formula is easier to use.

### 3. PURE SUBSTANCES WITH LIQUID-VAPOR PHASES

Use the tables for water/steam and refrigerant (R-134a) just as you did with energy.

For **saturated liquid**:  $s = s_f @ P_{sat}, T_{sat}$  (A-4, A-5, A-11, A-12)

For **saturated vapor**:  $s = s_g @ P_{sat}, T_{sat}$  (A-4, A-5, A-11, A-12)

For **vaporization or condensation from saturated liquid ↔ saturated vapor**:  $\Delta s = s_{fg} @ P_{sat}, T_{sat}$  (A-4, A-5, A-11, A-12)

For **superheated vapor**:  $s = s @ P, T$  (A-6, A-13)

For **saturated liquid-vapor mixture**:  $s = x(s_{fg}) + s_f @ P_{sat}, T_{sat}$

For compressed liquid:  $s_{CL} \approx s_f @ T_{CL}$

The specific entropy of a substance (kJ/kg-K) is independent of T, P, v, u, h and with one other independent intensive property determines the complete state of a simple compressible system.

### 4. CYCLES

$$\Delta S = 0$$