

ESO201A : THERMODYNAMICS

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Lecture 17

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Extension of Clausius equation to quasi-static irreversible process :

Recall that in the last lecture, we had considered a quasi-static irreversible process for which we can use Clausius equation for change of entropy :

$$dS = \left(\frac{dQ_{in}}{T} \right)_{\text{quasi-static}}$$

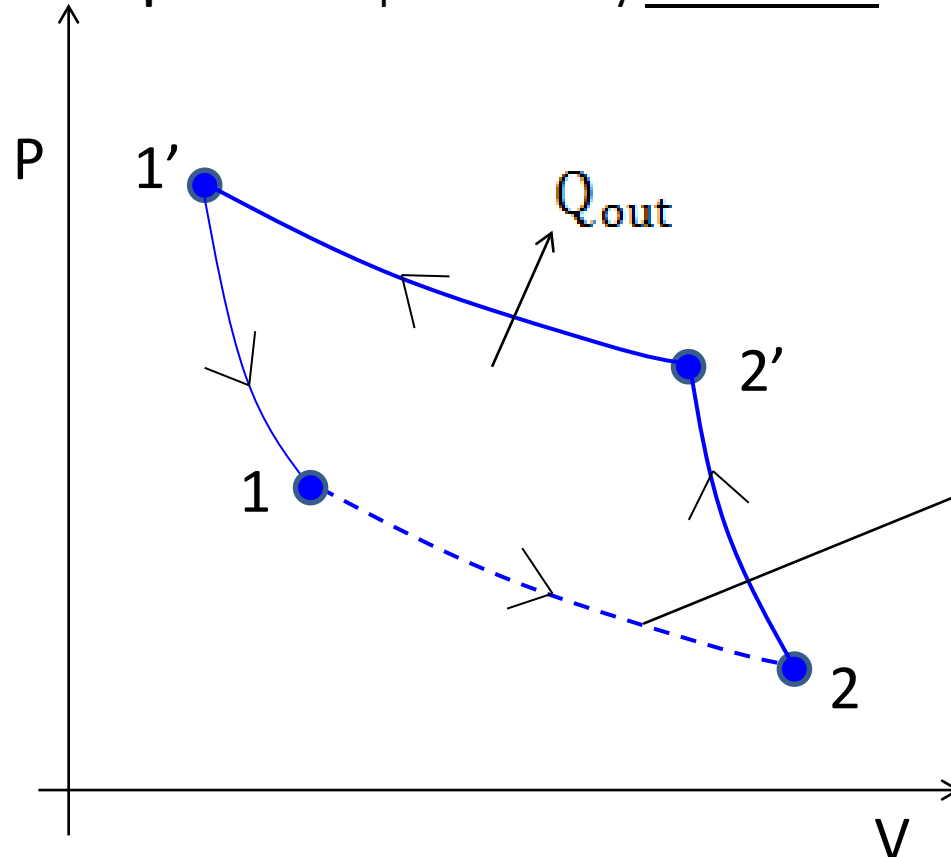
Lets recall the conditions under which we can apply the above equation for a quasi-static irreversible process. The **necessary conditions** for above equation to be applicable are :

- (1) the system must be in a state of **internal equilibrium** throughout. This condition also implies that internal pressure must be same as external pressure (pressure difference if any is infinitesimal and hence can be neglected). Note that pressure may change during the process.
- (2) Further, **temperature** must be **uniform** at any given stage of the process, though it may change during the process.

Adiabatic irreversible process on a P-V diagram

Recall that in the last lecture, we had considered a cycle in which gas undergoes adiabatic irreversible expansion from (1) to (2) and reversible compression from (2) to (1). The cycle was represented on P-V diagram as shown below.

Note that the **dashed curve** from (1) to (2) is just a representation of the irreversible process. It is **not the actual path**. Area under this dashed curve is NOT equal to the work done in the process. **Actual paths** are represented by **solid curves**.



Dashed curve is NOT the actual path.

Area under the dashed curve is NOT equal to work done during (1) → (2) process

1 → 2 : Adiabatic irreversible path

Increase of entropy principle

In the last lecture we had discussed statement (5) of second law applicable to adiabatic processes .

Note that if there is no energy transfer in the form of work, then the system can be treated as an isolated system. From statement (5) it follows that :

The entropy of an isolated system increase in an irreversible (natural) process and remains constant in a reversible process.

This is also known as “**Increase of entropy principle**”. This is sixth statement of Second law that we have learnt in this course.

Entropy change :

System together with all of the thermal energy reservoirs form an adiabatic system.

Applying fifth statement of Second law (for adiabatic process) :

$$(dS_{\text{system}} + dS_{\text{surr.}}) \geq 0$$

Assuming that surrounding undergo quasi-static processes such that surroundings are in internal equilibrium throughout the process and temperature is uniform throughout the process, we can Apply Clausius equation to surroundings. If dQ_{in} is the amount of heat transferred to the system from the surroundings, then

$$dS_{\text{surr.}} = - \left(\frac{dQ_{\text{in}}}{T} \right)$$

Entropy change :

Substituting entropy change of surroundings in the expression for total entropy change (see last slide), we get

$$dS_{\text{system}} - \left(\frac{dQ_{\text{in}}}{T} \right) \geq 0$$

$$\text{(OR)} \quad dS_{\text{system}} \geq \left(\frac{dQ_{\text{in}}}{T} \right)$$

Here the equality applies to a reversible process. For the entire adiabatically isolated system which consists of system + surroundings (see last slide) the total entropy change is positive (irreversible process) or zero (reversible process). The total entropy change is also known as entropy generated which is positive or zero. Thus,

$$dS_{\text{gen}} = (dS_{\text{system}} + dS_{\text{surr.}}) \geq 0$$

Entropy change :

The equations on the previous two slides were for infinitesimal changes. For a finite change, we can integrate those relations to obtain the following:

$$\Delta S_{\text{system}} \geq \int_1^2 \left(\frac{dQ_{\text{in}}}{T} \right)$$

$$\Delta S_{\text{gen}} = (\Delta S_{\text{system}} + \Delta S_{\text{surr.}}) \geq 0$$

Here the equality applies for a reversible process. Both of these results are derived from Second law applied to adiabatic processes.

Gibbs equation :

Consider a process of a pure substance in which the only form of work is that due to change of volume. Then, as per first law

$$dU = dQ_{in} - P_{ext} dV$$

If the process is such that system is in internal equilibrium throughout the process. Then we can apply Clausius equality :

$$dS = \frac{dQ_{in}}{T} \implies dQ_{in} = T dS$$

$$\text{Also, } P_{ext} = P$$

Substituting these in the first law equation, we get

$$\boxed{dU = T dS - P dV}$$

This is known as Gibbs equation.

Gibbs equation :

Consider a process between two equilibrium states of a pure substance. Then, the change in internal energy between these states is given by

$$\Delta U = \int_1^2 T \, dS - \int_1^2 P \, dV$$

The important point to note is that this equation only contains quantities that are functions of state. Hence the equation is valid **even if process is not quasi-static**.

However, the integral over the ($T \, dS$) on the right hand side can be equated to heat absorbed in the process **ONLY IF** the process is quasi-static (system is in internal equilibrium and temperature is uniform throughout the process)

Also the integral over ($P \, dV$) on the right hand side can be equated to work done by the system **ONLY IF** the process is quasi-static.

Entropy changes of pure substances :

One can invert Gibbs equation on previous slides to obtain the entropy change between two equilibrium states of a pure substance :

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

$$\Delta S = \int_1^2 \frac{1}{T}dU + \int_1^2 \frac{P}{T}dV$$

These equations are valid even if the process between the two equilibrium states is irreversible or non quasi-static.

Enthalpy and entropy changes of pure substances :

One can use Gibbs equation on previous slides to obtain the enthalpy change between two equilibrium states of a pure substance :

$$dH = dU + PdV + V dP$$

Substituting Gibbs equation for dU , we get

$$dH = T dS + V dP$$

The above equation can be inverted to obtain change in entropy

$$dS = \frac{1}{T}dH - \frac{V}{T}dP$$

Specific entropy difference between two equilibrium states, can be obtained by dividing the above equation by mass and integrating:

$$s_2 - s_1 = \int_1^2 \frac{1}{T}dh - \int_1^2 \frac{v}{T}dP$$

Specific entropy changes of water and R-134a:

The specific entropy values (per unit mass basis) for subcooled, saturated, and superheated states of water are listed in Property tables. As a reference state, the entropy of the saturated liquid water at triple point (s_f) is arbitrarily assigned the value of zero.

Saturated water—Temperature table

Temp., T °C	Sat. press., P_{sat} kPa	Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, $\text{kJ/kg}\cdot\text{K}$		
		Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g	Sat. liquid, s_f	Evap., s_{fg}	Sat. vapor, s_g
0.01	0.6117	0.001000	206.00	0.000	2374.9	2374.9	0.001	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	0.001000	147.03	21.019	2360.8	2381.8	21.020	2489.1	2510.1	0.0763	8.9487	9.0249
10	1.2281	0.001000	106.32	42.020	2346.6	2388.7	42.022	2477.2	2519.2	0.1511	8.7488	8.8999
15	1.7057	0.001001	77.885	62.980	2332.5	2395.5	62.982	2465.4	2528.3	0.2245	8.5559	8.7803
20	2.3392	0.001002	57.762	83.913	2318.4	2402.3	83.915	2453.5	2537.4	0.2965	8.3696	8.6661

Reference value

For a mixture of saturated liquid and saturated vapor, specific entropy can be calculated as :

$$s = (1 - X)s_f + Xs_g$$

(OR) $s = s_f + X s_{fg}$

Specific entropy changes of water and R-134a:

Similarly, specific entropy changes of R-134a (refrigerent can be obtained) from the corresponding property tables (A-11 to A-13). Here saturated liquid at -40 °C is taken as reference state, i.e., the specific entropy in this state is assigned the value of 0.

TABLE A-11

Saturated refrigerant-134a—Temperature table

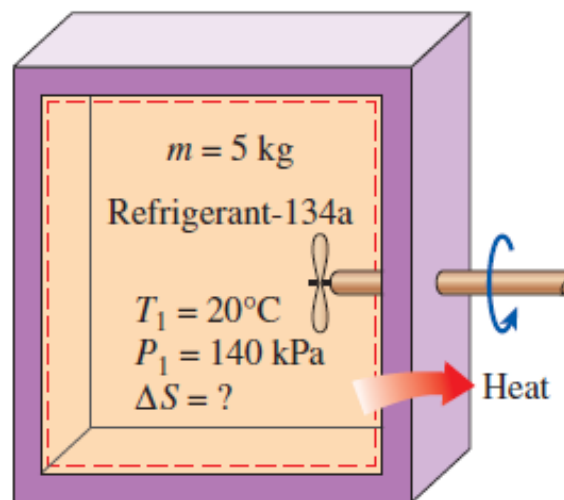
Temp., <i>T</i> °C	Sat. press., <i>P</i> _{sat} kPa	Specific volume, m ³ /kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg·K		
		Sat. liquid, <i>v</i> _f	Sat. vapor, <i>v</i> _g	Sat. liquid, <i>u</i> _f	Evap., <i>u</i> _{fg}	Sat. vapor, <i>u</i> _g	Sat. liquid, <i>h</i> _f	Evap., <i>h</i> _{fg}	Sat. vapor, <i>h</i> _g	Sat. liquid, <i>s</i> _f	Evap., <i>s</i> _{fg}	Sat. vapor, <i>s</i> _g
-40	51.25	0.0007054	0.36081	-0.036	207.40	207.37	0.000	225.86	225.86	0.00000	0.96866	0.96866
-38	56.86	0.0007083	0.32732	2.475	206.04	208.51	2.515	224.61	227.12	0.01072	0.95511	0.96584
-36	62.95	0.0007112	0.29751	4.992	204.67	209.66	5.037	223.35	228.39	0.02138	0.94176	0.96315
-34	69.56	0.0007142	0.27090	7.517	203.29	210.81	7.566	222.09	229.65	0.03199	0.92859	0.96058
-32	76.71	0.0007172	0.24711	10.05	201.91	211.96	10.10	220.81	230.91	0.04253	0.91560	0.95813

Reference value

As in the case of other properties, we can approximate specific entropy of any compressed liquid (such as water or R-134a) as follows :

$$s_{@T,P}(\text{compressed liquid}) \approx s_{f@T}$$

A rigid tank contains 5 kg of refrigerant-134a initially at 20°C and 140 kPa. The refrigerant is now cooled while being stirred until its pressure drops to 100 kPa. Determine the entropy change of the refrigerant during this process.



Recognizing that the specific volume remains constant during this process, the properties of the refrigerant at both states are

$$\text{State 1:} \quad \left. \begin{array}{l} P_1 = 140 \text{ kPa} \\ T_1 = 20^\circ\text{C} \end{array} \right\} \begin{array}{l} s_1 = 1.0625 \text{ kJ/kg}\cdot\text{K} \\ v_1 = 0.16544 \text{ m}^3/\text{kg} \end{array}$$

$$\text{State 2:} \quad \left. \begin{array}{l} P_2 = 100 \text{ kPa} \\ (v_2 = v_1) \end{array} \right\} \begin{array}{l} v_f = 0.0007258 \text{ m}^3/\text{kg} \\ v_g = 0.19255 \text{ m}^3/\text{kg} \end{array}$$

The refrigerant is a saturated liquid–vapor mixture at the final state since $v_f < v_2 < v_g$ at 100 kPa pressure. Therefore, we need to determine the quality first:

$$x_2 = \frac{v_2 - v_f}{v_{fg}} = \frac{0.16544 - 0.0007258}{0.19255 - 0.0007258} = 0.859$$

Thus,

$$s_2 = s_f + x_2 s_{fg} = 0.07182 + (0.859)(0.88008) = 0.8278 \text{ kJ/kg}\cdot\text{K}$$

Then, the entropy change of the refrigerant during this process is

$$\begin{aligned}\Delta S &= m(s_2 - s_1) = (5 \text{ kg})(0.8278 - 1.0625) \text{ kJ/kg}\cdot\text{K} \\ &= -1.173 \text{ kJ/K}\end{aligned}$$

Discussion The negative sign indicates that the entropy of the system is decreasing during this process. This is not a violation of the second law, however, since it is the *entropy generation* S_{gen} that cannot be negative.

Specific entropy changes of ideal gases :

Dividing the expression for the entropy difference (see slide 10) by total mass of the pure substance, we get

$$s_2 - s_1 = \int_1^2 \frac{1}{T} du + \int_1^2 \frac{P}{T} dv$$

As we have learnt in previous lectures, for an ideal gas $du = C_v dT$

Also, as per ideal gas law, $P v = R T$

Substituting these relations in the expression for the specific change in entropy, we get

$$s_2 - s_1 = \int_1^2 \frac{C_v}{T} dT + R \ln \left(\frac{v_2}{v_1} \right)$$

Here, C_v is the specific heat of the ideal gas at constant volume

Specific entropy changes of ideal gases :

Assuming C_v to be constant over the temperature range from T_1 to T_2 , the expression on the last slide can be simplified to :

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

One can also calculate, specific entropy changes of ideal gases using the following relation:

$$s_2 - s_1 = \int_1^2 \frac{1}{T} dh - \int_1^2 \frac{v}{T} dP$$

Substituting $dh = C_p dT$ and the ideal gas equation of state , we get

$$s_2 - s_1 = \int_1^2 \frac{C_p}{T} dT - R \ln \left(\frac{P_2}{P_1} \right)$$

If we assume C_p to be constant, above equation simplifies to :

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

Specific entropy changes of ideal gases :

If we want to calculate the entropy difference rigorously, i.e., without considering C_p to be constant, then we make use of ideal gas property tables (Table A-17 to A-24).

TABLE A-17

Ideal-gas properties of air

T K	h kJ/kg	P_r	u kJ/kg	v_r	s° kJ/kg·K
200	199.97	0.3363	142.56	1707.0	1.29559
210	209.97	0.3987	149.69	1512.0	1.34444
220	219.97	0.4690	156.82	1346.0	1.39105
230	230.02	0.5477	164.00	1205.0	1.43557
240	240.02	0.6355	171.13	1084.0	1.47824

Here $s^\circ(T)$ is a function of temperature and it is equal to the following integral :

$$s^\circ(T) = \int_0^T \frac{C_p}{T} dT$$

Specific entropy changes of ideal gases :

Thus, for a change of temperature from T_1 to T_2 , we have

$$s^o(T_2) - s^o(T_1) = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

Substituting this relation in the following general relation for ideal gases

$$s_2 - s_1 = \int_1^2 \frac{C_P}{T} dT - R \ln \left(\frac{P_2}{P_1} \right)$$

we get,

$$s_2 - s_1 = [s^o(T_2) - s^o(T_1)] - R \ln \left(\frac{P_2}{P_1} \right)$$

Here the entropy values on the right hand side are obtained from ideal gas property tables (A-17 to A-24). The above equation enables rigorous calculations of entropy changes in ideal gases.

Air is compressed from an initial state of 100 kPa and 17°C to a final state of 600 kPa and 57°C. Determine the entropy change of air during this compression process by using (a) property values from the air table and (b) average specific heats.

SOLUTION Air is compressed between two specified states. The entropy change of air is to be determined by using tabulated property values and also by using average specific heats.

(a) The properties of air are given in the air table (Table A–17). Reading s° values at given temperatures and substituting, we find

$$\begin{aligned}s_2 - s_1 &= s_2^\circ - s_1^\circ - R \ln \frac{P_2}{P_1} \\&= [(1.79783 - 1.66802) \text{ kJ/kg}\cdot\text{K}] - (0.287 \text{ kJ/kg}\cdot\text{K}) \ln \frac{600 \text{ kPa}}{100 \text{ kPa}} \\&= \mathbf{-0.3844 \text{ kJ/kg}\cdot\text{K}}\end{aligned}$$

(b) The entropy change of air during this process can also be determined approximately from Eq. 7–34 by using a c_p value at the average temperature of 37°C (Table A–2b) and treating it as a constant:

$$\begin{aligned}s_2 - s_1 &= c_{p,\text{avg}} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \\&= (1.006 \text{ kJ/kg}\cdot\text{K}) \ln \frac{330 \text{ K}}{290 \text{ K}} - (0.287 \text{ kJ/kg}\cdot\text{K}) \ln \frac{600 \text{ kPa}}{100 \text{ kPa}} \\&= \mathbf{-0.3842 \text{ kJ/kg}\cdot\text{K}}\end{aligned}$$

Specific entropy changes of liquids and solids :

If the values of specific entropy are not tabulated for specific liquid or a specific solid, we can estimate the entropy changes using following method. Recall that liquids and solids are generally considered as incompressible, i.e., the specific volume does not change significantly with pressure at constant temperature. We can then simplify the following relation for entropy change

$$s_2 - s_1 = \int_1^2 \frac{1}{T} du + \int_1^2 \frac{P}{T} dv$$

Substituting $dv \approx 0$ (incompressible substance), $C_p \approx C_v = C$, and $dU = C dT$ we get

$$s_2 - s_1 = \int_1^2 \frac{C(T)}{T} dT$$

Considering $C(T) \approx C_{avg}$ (constant), we get

$$s_2 - s_1 = C_{avg} \ln \left(\frac{T_2}{T_1} \right)$$