MAE 3302— Engineering Thermodynamics II — Spring 2021 — Entropy and Isentropic Processes (assuming a thermally perfect gas after Eq. (4))

Recall:

First Law:

$$\boxed{\mathrm{d}U = \delta Q_{\text{in}} + \delta W_{\text{in}}}$$

Allowing only pV work interaction

$$\delta W_{\text{in}} = -p\mathrm{d}V$$

Second Law:

$$\boxed{\mathrm{d}S = \left(\frac{\delta Q}{T}\right) + \delta \mathscr{P}_s \quad \text{where} \quad \delta \mathscr{P}_s \geq 0}$$

If internally reversible (i.e., production equals zero)

$$\mathrm{d}S = \left(\frac{\delta Q}{T}\right)_{\text{IntRev}} \quad \text{or} \quad T\mathrm{d}S = \delta Q_{\text{IntRev}}$$

Combining

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V$$

rearranging:

$$T\mathrm{d}S = \mathrm{d}U - p\mathrm{d}V \tag{1}$$

or

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}U + \frac{p}{T}\mathrm{d}V$$

and on a per unit mass basis:

$$\boxed{\mathrm{d}s = \frac{1}{T}\mathrm{d}u + \frac{p}{T}\mathrm{d}v} \tag{2}$$

Similarly, with the definition of enthalpy:

$$H \equiv U + pV$$

and differentiating (using the product rule):

$$\mathrm{d}H = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p$$

Combining with Eq. (1) yields:

$$T\mathrm{d}S = \mathrm{d}H - V\mathrm{d}p \tag{3}$$

or

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}H - \frac{V}{T}\mathrm{d}p$$

and on a per unit mass basis:

$$\boxed{\mathrm{d}s = \frac{1}{T}\mathrm{d}h - \frac{v}{T}\mathrm{d}p} \tag{4}$$

Both Eqs. (2) and (4) are general (reversible or irreversible, assuming only pV work and non-reacting).

In general, $h = h(T, p)$, so:

$$\mathrm{d}h = \left.\frac{\partial h}{\partial T}\right|_p \mathrm{d}T + \left.\frac{\partial h}{\partial p}\right|_T \mathrm{d}p$$

For a non-reaction gas, if we further assume that the gas is thermally perfect (i.e., $u = u(T)$ and $h = h(T)$) and recalling that $c_v \equiv \frac{\partial u}{\partial T}|_v$ and $c_p \equiv \frac{\partial h}{\partial T}|_p$, we may write:

$$\mathrm{d}u = c_v \mathrm{d}T \quad \text{and} \quad \mathrm{d}h = c_p \mathrm{d}T$$

Note that $c_v = c_v(T)$ and $c_p = c_p(T)$.

For a thermally perfect gas:

$$pv = RT \quad \text{or} \quad pV = mRT \quad \text{or} \quad pV = nKT \quad \text{or} \quad pv = \frac{R_\mathrm{u}}{\mathrm{M}}T$$

In other words:

$$\frac{p}{T} = \frac{R}{v} \quad \text{and} \quad \frac{v}{T} = \frac{R}{p}$$

Equation (2) may be then written:

$$\boxed{\mathrm{d}s = \frac{1}{T} c_v \mathrm{d}T + \frac{R}{v}\mathrm{d}v} \tag{5}$$

and Eq. (4) may be written:

$$\boxed{\mathrm{d}s = \frac{1}{T} c_p \mathrm{d}T - \frac{R}{p}\mathrm{d}p} \tag{6}$$

If we know $c_v(T)$ and $c_p(T)$, Eqs. (5) and (6) may be integrated from some reference state (see for example Table A-22 for integrated properties of air).

$$\Delta s = s_2 - s_1 = \int_1^2 \frac{1}{T} c_p(T)\,\mathrm{d}T - R\ln\frac{p_2}{p_1} = s^0(T_2) - s^0(T_1) - R\ln\frac{p_2}{p_1}$$

TABLE A-22 **Ideal Gas Properties of Air**

T(K), h and u (kJ/kg), $s°$ (kJ/kg · K)											
				when $\Delta s = 0$[1]						when $\Delta s = 0$	
T	h	u	$s°$	p_r	v_r	T	h	u	$s°$	p_r	v_r
200	199.97	142.56	1.29559	0.3363	1707.	450	451.80	322.62	2.11161	5.775	223.6
210	209.97	149.69	1.34444	0.3987	1512.	460	462.02	329.97	2.13407	6.245	211.4
220	219.97	156.82	1.39105	0.4690	1346.	470	472.24	337.32	2.15604	6.742	200.1
230	230.02	164.00	1.43557	0.5477	1205.	480	482.49	344.70	2.17760	7.268	189.5
240	240.02	171.13	1.47824	0.6355	1084.	490	492.74	352.08	2.19876	7.824	179.7
250	250.05	178.28	1.51917	0.7329	979.	500	503.02	359.49	2.21952	8.411	170.6
260	260.09	185.45	1.55848	0.8405	887.8	510	513.32	366.92	2.23993	9.031	162.1
270	270.11	192.60	1.59634	0.9590	808.0	520	523.63	374.36	2.25997	9.684	154.1
280	280.13	199.75	1.63279	1.0889	738.0	530	533.98	381.84	2.27967	10.37	146.7
285	285.14	203.33	1.65055	1.1584	706.1	540	544.35	389.34	2.29906	11.10	139.7
290	290.16	206.91	1.66802	1.2311	676.1	550	554.74	396.86	2.31809	11.86	133.1
295	295.17	210.49	1.68515	1.3068	647.9	560	565.17	404.42	2.33685	12.66	127.0
300	300.19	214.07	1.70203	1.3860	621.2	570	575.59	411.97	2.35531	13.50	121.2
305	305.22	217.67	1.71865	1.4686	596.0	580	586.04	419.55	2.37348	14.38	115.7
310	310.24	221.25	1.73498	1.5546	572.3	590	596.52	427.15	2.39140	15.31	110.6
315	315.27	224.85	1.75106	1.6442	549.8	600	607.02	434.78	2.40902	16.28	105.8
320	320.29	228.42	1.76690	1.7375	528.6	610	617.53	442.42	2.42644	17.30	101.2
325	325.31	232.02	1.78249	1.8345	508.4	620	628.07	450.09	2.44356	18.36	96.92
330	330.34	235.61	1.79783	1.9352	489.4	630	638.63	457.78	2.46048	19.84	92.84
340	340.42	242.82	1.82790	2.149	454.1	640	649.22	465.50	2.47716	20.64	88.99
350	350.49	250.02	1.85708	2.379	422.2	650	659.84	473.25	2.49364	21.86	85.34
360	360.58	257.24	1.88543	2.626	393.4	660	670.47	481.01	2.50985	23.13	81.89
370	370.67	264.46	1.91313	2.892	367.2	670	681.14	488.81	2.52589	24.46	78.61
380	380.77	271.69	1.94001	3.176	343.4	680	691.82	496.62	2.54175	25.85	75.50
390	390.88	278.93	1.96633	3.481	321.5	690	702.52	504.45	2.55731	27.29	72.56
400	400.98	286.16	1.99194	3.806	301.6	700	713.27	512.33	2.57277	28.80	69.76
410	411.12	293.43	2.01699	4.153	283.3	710	724.04	520.23	2.58810	30.38	67.07
420	421.26	300.69	2.04142	4.522	266.6	720	734.82	528.14	2.60319	32.02	64.53
430	431.43	307.99	2.06533	4.915	251.1	730	745.62	536.07	2.61803	33.72	62.13
440	441.61	315.30	2.08870	5.332	236.8	740	756.44	544.02	2.63280	35.50	59.82

1. p_r and v_r data for use with Eqs. 6.41 and 6.42, respectively.

Figure 1: Thermally perfect gas properties of air

Example: What is the enthalpy of air (per unit mass) at 660 K and 100 atm?

Table A-22 $\Rightarrow h = 670.47\,\mathrm{kJ/kg}$

CoolProp at 1 Pa $\Rightarrow h = 671.044\,\mathrm{kJ/kg}$

CoolProp at 1 atm $\Rightarrow h = 671.051\,\mathrm{kJ/kg}$

CoolProp at 100 atm $\Rightarrow h = 672.334\,\mathrm{kJ/kg}$

Percent change from 1 atm to 100 atm = 0.1908%, not very much.

Example: What is the entropy of air (per unit mass) at 660 K and 100 atm?

Table A-22 $\Rightarrow s^0 = 2.50985\,\mathrm{kJ/(kg\ K)}$

But wait, that is not s!

$$s(T,p) = s^0(T) - R\ln\frac{p}{p_{\mathrm{ref}}}$$

Recall $R_{\mathrm{air}} = 0.287\,\mathrm{kJ/kg}$ and, often, p_{ref} is taken as 1 atm.

So, for our example:

$$s(T,p) = 2.50985 - 0.287\ln\frac{100}{1} = 1.18817\,\frac{\mathrm{kJ}}{\mathrm{kg\cdot K}}$$

Typically, though, we are interested in the change of entropy during a process:

Example: What is the change in entropy of air (per unit mass) from 300 K and 0.7 atm to 660 K and 100 atm?

Using:

$$s_2(T_2,p_2) - s_1(T_1,p_1) = s_2^0(T_2) - s_1^0(T_1) - R\ln\frac{p_2}{p_1} \tag{7}$$

Yielding:

$$s_2(T_2,p_2) - s_1(T_1,p_1) = 2.50985 - 1.70203 - 0.287\ln\frac{100}{0.7} = -0.61623\,\frac{\mathrm{kJ}}{\mathrm{kg\cdot K}}$$

CoolProp $\Rightarrow \Delta s = -0.625063\,\mathrm{kJ/(kg\ K)}$

Isentropic process (TPG)

If a process is idealized as adiabatic and reversible, then it is isentropic. For thermally perfect gases these processes can be simplified from Eq. (7), setting the left-hand side to zero. Dividing by R, exponentiating, and rearranging:

$$\frac{p_2}{p_1} = \frac{\exp\left[s^0(T_2)/R\right]}{\exp\left[s^0(T_1)/R\right]} = \frac{p_{\mathrm{r}2}}{p_{\mathrm{r}1}}$$

where $p_{\mathrm{r}1} \equiv \exp\left[s^0(T_1)/R\right]$ is the relative pressure (NOT the reduced pressure used in our compressibility diagrams).

Using the thermally perfect gas state equation we may also write:

$$\frac{v_2}{v_1} = \left[\frac{RT_2}{p_{\mathrm{r}2}}\right]\left[\frac{p_{\mathrm{r}1}}{RT_1}\right] = \frac{v_{\mathrm{r}2}}{v_{\mathrm{r}1}}$$

Entropy change for a calorically perfect gas:

If we further assume that $c_v(T)$ and $c_p(T)$ and nearly constant (i.e., a calorically perfect gas), then the integrations is easy:

$$\boxed{s_2 - s_1 = c_v \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{v_2}{v_1}\right)} \tag{8}$$

and

$$\boxed{s_2 - s_1 = c_p \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{p_2}{p_1}\right)} \tag{9}$$

Often, we study idealized processes which are internally reversible and adiabatic, and therefore, isentropic.

Isentropic relationships (isentropic, TPG, and CPG)

For processes that are internally reversible and adiabatic and if the working fluid may be modeled as both thermally and calorically perfect, then we may derive some very simple but extremely useful relationships.

Consistent with our current assumptions, we may start from Eq. (8) or Eq. (9). For an isentropic process, Eq. (8) may be written:

$$0 = c_v \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{v_2}{v_1}\right)$$

or

$$\frac{c_v}{R}\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{v_1}{v_2}\right) = \ln\left(\frac{\rho_2}{\rho_1}\right) \tag{10}$$

Given the ratio of specific heats, $\gamma \equiv c_p/c_v$ and that for a thermally perfect gas:

$$c_p = c_v + R$$

we find that:

$$\frac{c_v}{R} = \frac{1}{\gamma - 1}$$

As a result, Eq. (10) may be written:

$$\frac{1}{\gamma-1}\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{v_1}{v_2}\right) = \ln\left(\frac{\rho_2}{\rho_1}\right)$$

Exponentiating:

$$\boxed{\left(\frac{T_2}{T_1}\right)^{\left(\frac{1}{\gamma-1}\right)} = \left(\frac{v_1}{v_2}\right) = \left(\frac{\rho_2}{\rho_1}\right)} \tag{11}$$

Similarly, an isentropic process and Eq. (9) yields:

$$0 = c_p \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{p_2}{p_1}\right)$$

or

$$\frac{c_p}{R}\ln\left(\frac{T_2}{T_1}\right) = \ln\left(\frac{p_2}{p_1}\right)$$

With the definition of γ and the relation $c_p = c_v + R$, we find:

$$\frac{c_p}{R} = \frac{\gamma}{\gamma-1}$$

Substituting and exponentiating yields:

$$\boxed{\left(\frac{T_2}{T_1}\right)^{\left(\frac{\gamma}{\gamma-1}\right)} = \left(\frac{p_2}{p_1}\right)} \tag{12}$$

Combining Eqs. (11) and (13), we can find a third isentropic relationships:

$$\boxed{\left(\frac{p_2}{p_1}\right) = \left(\frac{\rho_2}{\rho_1}\right)^{\gamma}} \tag{13}$$

<u>Example:</u>

Air initially at 300 K and 1 atm is compressed in a reversible, adiabatic process to 1/10 its initial volume.

Find the final temperature and pressure of the air.