

# Aerospace Propulsion

## Lecture 2

### Thermodynamics Review

# Thermodynamics Review

- Properties of Gases
- The First Law
- The Second Law
- Thermal Efficiency and Cycles

# State Properties

- **Extensive** properties depend on the system size
  - Examples: volume ( $V$ ), energy ( $E$ )
  - *Generally*, use an uppercase letter
- **Intensive** properties are independent of the system size
  - Examples: temperature ( $T$ ), specific volume ( $v$ ), specific energy ( $e$ )
  - *Generally*, use a lowercase letter...
  - Mass-based – regular letter:  $[e] = \text{J/kg}$
  - Mole-based – letter with overbar:  $[\bar{e}] = \text{J/mol}$ 
    - **\*NOTE\***: Sutton does not use an overbar

# Properties of Gases

- Ideal Gas Law

- $pv = RT$  or  $p = \rho RT$
- Specific gas constant:  $R = \bar{R}/\bar{m}$
- Universal gas constant:  $\bar{R} = 8.314 \text{ J/mol-K}$

Molar mass  $\frac{\text{g}}{\text{mol}}$



$$R_{O_2} = \frac{\bar{R}}{\bar{m}_{O_2}} = \frac{\bar{R}}{2 \bar{m}_O}$$

$$= \frac{8.314 \frac{\text{J}}{\text{mol-K}}}{2 (16 \frac{\text{g}}{\text{mol}})}$$

- Internal Energy and Enthalpy

- Only a function of temperature for ideal gases

$$du = c_v(T) dT$$

$$dh = c_p(T) dT$$

# Properties of Gases

- Specific Heats

- $c_v = \left( \frac{\partial u}{\partial T} \right)_v$

- $c_p = \left( \frac{\partial h}{\partial T} \right)_p$

Which is larger,  $c_p$  or  $c_v$ ? How does this affect how much temperature change a system would experience at constant pressure vs. constant volume?

- Useful relationships

- $c_p - c_v = R$

- $\gamma = c_p / c_v$



# The First Law of Thermodynamics

## • Conservation of Energy

1. Change in system energy
2. Heat transfer into system
3. Work done by system

$$\underbrace{de}_{\textcircled{1}} = \underbrace{\delta q}_{\textcircled{2}} - \underbrace{\delta w}_{\textcircled{3}}$$

Remember there is a difference between path-dependent quantities ( $\delta q$  and  $\delta w$ ) and path-independent quantities ( $de$ )!

- Specific Energy:  $e = u + k + \cancel{\phi}$ 
    - Internal energy:  $u$
    - Kinetic energy:  $k = \frac{1}{2} \mathbf{v} \cdot \mathbf{v}$
- $\swarrow$  Neglected because small term  
 $\nwarrow$  Will be neglected relative to others in this course. Why?

# The First Law of Thermodynamics

- Compression/Expansion Work

- Reversible (no friction)
- $\delta w = p dv$
- First Law:  $\delta q = \underbrace{du + p dv}$

- Enthalpy

- $h \equiv u + pv = (\text{internal energy}) + (\text{flow work})$
- First Law:  $\delta q = dh - v dp$

$$h = u + pV$$

$$dh = du + p dv + v dp$$

$$dh - v dp = \underbrace{du + p dv}$$

$$\delta q = dh - v dp$$

Why would we define enthalpy? Is it ever more useful than internal energy?

NOTE: Kinetic energy is neglected on this slide

# The First Law of Thermodynamics

- Types of Processes
  - Adiabatic ( $\delta q = 0$ )
    - $du = -pdv$
    - $dh = vdp$
  - Isochoric/Isometric ( $dv = 0$ )
    - $du = \delta q$  ✓
  - Isobaric ( $dp = 0$ )
    - $dh = \delta q$  ✓
  - Isothermal ( $dT = 0$ )





# The First Law of Thermodynamics

- To evaluate internal energy and enthalpy for ideal gas

- $u = \int_{T_{ref}}^T c_v dT' + u(T_{ref})$

- $h = \int_{T_{ref}}^T c_p dT' + h(T_{ref})$

$$\begin{aligned} du &= c_v dT \\ \int_{u_{ref}}^u du' &= \int_{T_{ref}}^T c_v dT' \end{aligned}$$

$$u = u_{ref} + \int_{T_{ref}}^T c_v dT'$$

- Results of these integrals and reference states are tabulated
  - We'll primarily use the JANAF tables (more details soon)
- Often, we treat specific heats as constant (easy!)

$$\int_{T_{ref}}^T c_v dT' = c_v (T - T_{ref})$$

# The Second Law of Thermodynamics

- Reversible process
  - A process that can be reversed without leaving any trace on surroundings
- In a reversible system:

$$ds = \frac{\delta q}{T}$$

- Using earlier equations, can show

- $ds = c_v \frac{dT}{T} + R \frac{dv}{v}$  \*
- $ds = c_p \frac{dT}{T} - R \frac{dp}{p}$

$$ds = \frac{\delta q}{T} \quad ? \quad \delta q = du + p dv$$

$$ds = \frac{du}{T} + \frac{p dv}{T} \quad (1)$$

$$pV = RT$$
$$\frac{p}{T} = \frac{R}{v} \quad (2)$$

$$du = c_v dT \quad (3)$$

Combine  
1, 2, 3  
to get \*

# The Second Law of Thermodynamics

- Irreversible process

$$ds \geq \frac{\delta q}{T} \text{ or alternatively } ds = \frac{\delta q}{T} + \sigma^2$$

Entropy generation



- Examples
  - Friction
  - Heat transfer across finite temperature gradients
  - Chemical reactions
- Second Law dictates that processes occur in a certain direction

# The Second Law of Thermodynamics

$$ds = \frac{\delta q}{T} + \sigma^2 \Rightarrow \delta q = -T\sigma^2$$

- Isentropic Process ( $ds = 0$ )
  - *Technically* not required to be adiabatic ( $\delta q = 0$ ) or reversible ( $\sigma^2 = 0$ )
  - We will always treat isentropic processes as adiabatic and reversible
    - Inverse not necessarily true!
- Adiabatic systems that are not isentropic **must be** irreversible
  - Thus, these systems tend towards their maximum entropy state

$$\begin{aligned}\delta q &= 0 \\ \sigma^2 &> 0 \\ ds &\neq 0\end{aligned}$$

Why?

# The Second Law of Thermodynamics

- ideal gas)  
constant  $c_p$
- Isentropic processes of ideal gases
  - Assuming an ideal gas with constant specific heats

$$dS = c_p \frac{dT}{T} - R \frac{dp}{p}$$

Isentropic

$$0 = c_p \frac{dT}{T} - R \frac{dp}{p}$$

$$\frac{dT}{T} = \frac{R}{c_p} \frac{dp}{p}$$

$$\int_{T_1}^{T_2} \frac{dT}{T} = \frac{R}{c_p} \int_{p_1}^{p_2} \frac{dp}{p}$$

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

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

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

$$\frac{p_2}{p_1} = \left(\frac{v_1}{v_2}\right)^{\gamma}$$

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

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

$$R = c_p - c_v$$

$$\gamma = c_p / c_v$$

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

# The Second Law of Thermodynamics

- Evaluating Entropy

$$ds = c_p \frac{dT}{T} - R \frac{dp}{p} \quad s(T, P) = s(T_{ref}, P_{ref}) + \underbrace{\int_{T_{ref}}^T c_p \frac{dT'}{T'} - R \ln \frac{P}{P_{ref}}}_{\text{Handwritten annotations: } S - S_{ref}, c_p = f(T), R \ln \left( \frac{P}{P_{ref}} \right)}$$

Handwritten annotations for the integral term:

- $\int_{S_{ref}}^S ds' = \int_{T_{ref}}^T c_p \frac{dT'}{T'} - R \int_{P_{ref}}^P \frac{dp'}{p'}$
- $c_p = f(T)$  (indicated by a green arrow pointing to  $c_p$ )
- $R \ln \left( \frac{P}{P_{ref}} \right)$  (indicated by a blue bracket under the  $- R \ln \frac{P}{P_{ref}}$  term)

- As for internal energy and enthalpy, these quantities are tabulated  
or, assume constant specific heat

# JANAF Tables

- We derived enthalpy and entropy as:

$$h = \int_{T_{ref}}^T c_p dT' + h(T_{ref}) \qquad s(T, P) = s(T_{ref}, P_{ref}) + \int_{T_{ref}}^T c_p \frac{dT'}{T'} - R \ln \frac{P}{P_{ref}}$$

- How do we compute the various complex terms?
  - <https://janaf.nist.gov/>
  - Search for your gas (e.g., N2)

# JANAF Tables

$$h = \int_{T_{ref}}^T c_p dT' + h(T_{ref})$$

$$s(T, P) = s(T_{ref}, P_{ref}) + \int_{T_{ref}}^T c_p \frac{dT'}{T'} - R \ln \frac{P}{P_{ref}}$$

Table column	Mathematical term
T/K	Temperature in Kelvin
<b>a</b> $H - H^0(T_r)$	$\int_{T_{ref}}^T c_p dT'$
<b>b</b> $S^0$	$\int_{T_{ref}}^T c_p \frac{dT'}{T'}$

Per volume

Per mass

$$h = \bar{h} / \bar{m}$$

$$s = \bar{s} / \bar{m}$$

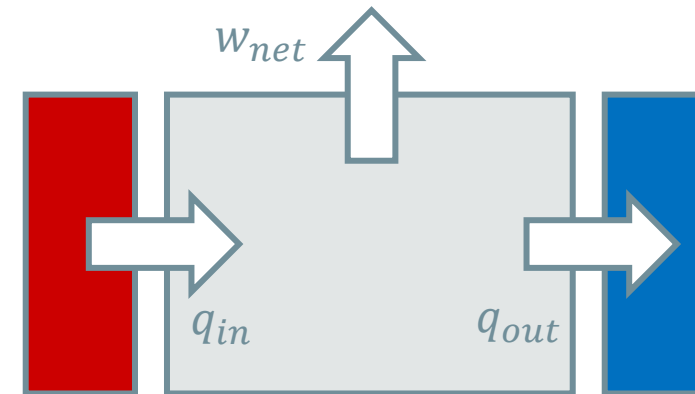
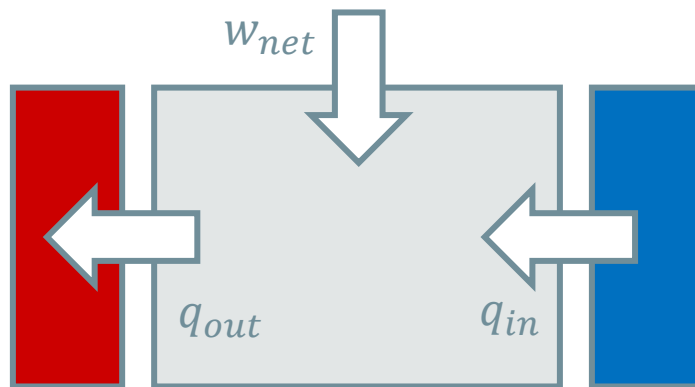
Nitrogen (N<sub>2</sub>)

		$T_{ref}$		$P_{ref}$		N <sub>2</sub> (ref)		
		Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$		Standard State Pressure = $p^\circ = 0.1 \text{ MPa}$				
		J·K <sup>-1</sup> mol <sup>-1</sup>			kJ·mol <sup>-1</sup>			
T/K	C <sub>p</sub> <sup>o</sup>	S <sup>o</sup>	-[G <sup>o</sup> -H <sup>o</sup> (T <sub>r</sub> )]/T	H-H <sup>o</sup> (T <sub>r</sub> )	Δ <sub>f</sub> H <sup>o</sup>	Δ <sub>f</sub> G <sup>o</sup>	log K <sub>f</sub>	
0	0.	0.			0.	0.	0.	
100	29.104	159.811			0.	0.	0.	
200	29.107	179.985	194.272	-2.857	0.	0.	0.	
250	29.111	186.481	192.088	-1.402	0.	0.	0.	
298.15	29.124	191.609	191.609	0.				
300	29.125	191.789	191.610	0.054	0.	0.	0.	
350	29.165	196.281	191.964	1.511	0.	0.	0.	
400	29.249	200.181	192.753	2.971	0.	0.	0.	
450	29.387	203.633	193.774	4.437	0.	0.	0.	
500	29.580	206.739	194.917	5.911	0.	0.	0.	



# Thermodynamic Cycles

- A thermodynamic cycle is a series of processes that returns a system to its initial state
  - Generally used to convert energy between different forms
    - Refrigeration cycle uses work input to move energy from cold to hot reservoir
    - Power cycle generates work output by moving energy from hot to cold reservoir



# Power Cycles Efficiency

- Thermodynamic Efficiency
  - For power cycles, we're interested in how much useful work we can extract from given heat input (e.g., from burning fuel)

For a cycle:

$$W_{net} = q_{net}$$

$$W_{net} = q_{in} - q_{out}$$

$$\eta = \frac{W_{net}}{q_{in}} = 1 - \frac{q_{out}}{q_{in}}$$

$$\eta = \frac{q_{in} - q_{out}}{q_{in}}$$

# Thermodynamic Process Example

- Consider a thermodynamic process with Oxygen ( $O_2$ ), assumed to be an ideal gas with variable specific heats
  - The gas begins at state 1 with  $T_1 = 298.15\text{ K}$  and  $p_1 = 200.0\text{ kPa}$
  - While keeping the volume constant, heat is added up to a final temperature of  $T_2 = 1000\text{ K}$
  - Determine  $h_2$ ,  $s_2$ , and  $q_{in}$

# Thermodynamic Process Example

Oxygen (O<sub>2</sub>)

O<sub>2</sub>(ref)

Enthalpy Reference Temperature =  $T_r = 298.15$  K

Standard State Pressure =  $p^\circ = 0.1$  MPa

		J·K <sup>-1</sup> mol <sup>-1</sup>		kJ·mol <sup>-1</sup>			
T/K	$C_p^\circ$	$S^\circ$	$-[G^\circ - H^\circ(T_r)]/T$	$H - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	log $K_f$
0	0.	0.	INFINITE	-8.683	0.	0.	0.
100	29.106	173.307	231.094	-5.779	0.	0.	0.
200	29.126	193.485	207.823	-2.868	0.	0.	0.
250	29.201	199.990	205.630	-1.410	0.	0.	0.
298.15	29.376	205.147	205.147	0.	0.	0.	0.
300	29.385	205.329	205.148	0.054	0.	0.	0.
350	29.694	209.880	205.506	1.531	0.	0.	0.
400	30.106	213.871	206.308	3.025	0.	0.	0.
450	30.584	217.445	207.350	4.543	0.	0.	0.
500	31.091	220.693	208.524	6.084	0.	0.	0.
600	32.090	226.451	211.044	9.244	0.	0.	0.
700	32.981	231.466	213.611	12.499	0.	0.	0.
800	33.733	235.921	216.126	15.835	0.	0.	0.
900	34.355	239.931	218.552	19.241	0.	0.	0.
1000	34.870	243.578	220.875	22.703	0.	0.	0.

$$R = R_{O_2} = \frac{\bar{R}}{\bar{M}_{O_2}} = \frac{8.314 \frac{J}{mol \cdot K}}{2(16 \frac{g}{mol})}$$

$$R = 259.84 \frac{J}{kg \cdot K}$$

$$V_1 = V_2 \quad *$$

Ideal gas Law

$$pV = RT$$

$$V_1 = \frac{RT_1}{p_1} = \frac{(259.84 \frac{J}{kg \cdot K})(298.15 K)}{(200,000 Pa)}$$

$$V_1 = 0.387 \text{ m}^3/kg$$

$$p_2 = \frac{RT_2}{V_2}$$

$$p_2 = \frac{(259.84 \frac{J}{kg \cdot K})(1000 K)}{(0.387 \text{ m}^3/kg)}$$

$$p_2 = 671,421 Pa$$

$$h = h_{ref} + \int_{T_{ref}}^T c_p dT'$$

$$h_1 = \int_{T_{ref}}^{298.15 K} c_p dT'$$

$$h_1 = \left(0 \frac{kJ}{mol}\right) \left(\frac{1}{\bar{M}_{O_2}}\right)$$

$$= \left(0 \frac{kJ}{mol}\right) \left(\frac{1}{0.032 \frac{kg}{mol}}\right) = 0 \frac{kJ}{kg}$$



$$h = \int_{T_{ref}}^T c_p dT' + h_{ref}$$

$$h_2 = \int_{T_{ref}}^{T_2=1000K} c_p dT'$$

$$h_2 = (22.703 \frac{kJ}{mol}) \left( \frac{1}{0.032 \frac{kg}{mol}} \right)$$

$$h_2 = 709.5 \frac{kJ}{kg}$$

$$S = S_{ref} + \int_{T_{ref}}^T c_p \frac{dT'}{T'} + R \ln \left( \frac{p}{p_{ref}} \right)$$

$$S = \bar{S} \Rightarrow \bar{S} = S \bar{M}$$

$$\bar{S} = \left[ \bar{M} \int_{T_{ref}}^T c_p \frac{dT'}{T'} + \bar{R} \right] \ln \left( \frac{p}{p_{ref}} \right)$$

= Table Value

Should be  
a minus  
sign

$$\bar{S}_2 = \left[ 243.598 \frac{J}{mol \cdot K} \right] + (8.314 \frac{J}{mol \cdot K}) \ln \left( \frac{691,424 Pa}{100,000 Pa} \right)$$

$$\bar{S}_2 = 227.75 \frac{J}{mol \cdot K}$$

$$S_2 = \frac{\bar{S}_2}{\bar{M}_{O_2}} = 7.11 \frac{kJ}{kg \cdot K}$$

Find  $q_{in}$

First Law

$$dh = \delta q + v dp$$

$$\delta q = dh - v dp$$

$$\int_1^2 \delta q = \int_1^2 dh - v \int_1^2 dp$$

$$q_{in} = (h_2 - h_1) - v(p_2 - p_1)$$

$$q_{in} = 527 \frac{kJ}{kg}$$