Unit Four – First Law for Ideal Gases

Mechanical Engineering 370

Thermodynamics

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Outline

- Quiz three solution
- Unit four – first law for ideal gases
  - Heat capacities, c_v and c_p are properties
  - For ideal gases $du = c_v dT$ and $dh = c_p dT$, regardless of path
  - For ideal gases $u = u(T)$ only and $h = u + Pv = u + RT = h(T)$ only
  - Solving first law problems with ideal gases

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Unit Four Goals

- As a result of studying this unit you should be able to
  - describe the path for a process and determine the work with greater confidence than you had after completing unit three
  - understand the heat capacities C_x (e.g. C_p and C_v) as $dQ = C_x dT$ in a "constant-x" process
  - use the *property* relations for ideal gases $du = c_v dT$ and $dh = c_p dT$ for ***any*** process

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Unit Four Goals Continued

- find changes in internal energy and enthalpy for an ideal gas where the heat capacity is constant or a function of temperature .
- use ideal gas tables to find changes in internal energy and enthalpy where the heat capacities are functions of temperature
- find internal energy changes for ideal gases as $\Delta h = \Delta u + R \Delta T$
- convert results from a per-unit-mole basis to a per-unit-mass basis and *vice versa*

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Unit Four Goals Continued

- be able to find other properties about a state when you know (or able to calculate) the internal energy or enthalpy
- be able to work problems using the first law, $Pv = RT$, $du = c_v dT$, and a path equation (may be iterative)
- use the equation $c_p - c_v = R$ to find c_p from c_v (and *vice versa*), which also applies to equations; if $c_p = a + bT + cT^2$, then $c_v = (a-R) + bT + cT^2$

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Why Use Ideal Gas?

- Simple equations
- Real gas behavior close to ideal gas for low pressure (or high temperature)
- Want P low compared to P_c or T high compared to T_c
  - Have seen that ideal gas gives good results for P-v-T data when $P < \sim 0.2P_c$ or $T > \sim 2T_c$
  - Will also see that this region gives good results for internal energy change, Δu

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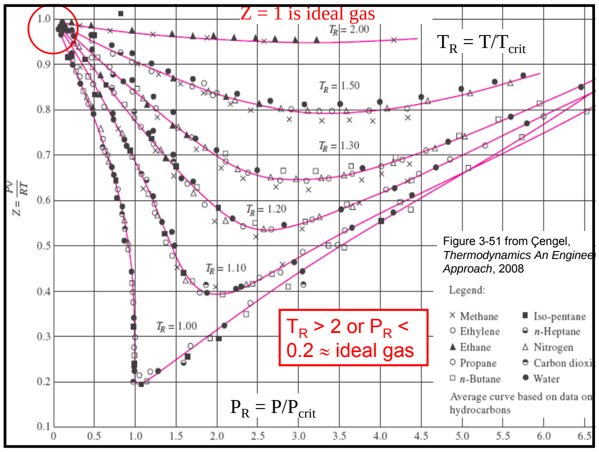

Heat Capacity

- Heat capacity, $C_x = mc_x$, gives heat transfer $dQ = C_xdT$ in constant x process
- Specific heat capacity, $c_x = C_x/m$ is a property
- Use c_v and c_p for constant volume and pressure, respectively
- For liquids and solids c_v and c_p are essentially the same
  - $dq = c_vdT$ at constant volume
  - $dq = c_pdT$ at constant pressure

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Ideal Gases

- For ideal gases, $du = c_vdT$, $dh = c_pdT$ regardless of path
- Note these differences
  - Path dependent heat transfer
    - $dq = c_vdT$ for constant volume only
    - $dq = c_pdT$ for constant pressure only
  - Path independent properties du and dh
- $\Delta u = \Delta U/m = \int c_vdT$, $\Delta h = \Delta H/m = \int c_pdT$
- $h = u + Pv = u + RT$ for ideal gases
  - $dh = du + RdT$ => $c_pdT = c_vdT + RdT$
  - $c_p = c_v + R$

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Is c_v for Constant Volume or Not?

- Depends on path and substance

Find	Equation	Path	Substance
dq	c_vdT	Constant volume	Any
dq	c_pdT	Constant pressure	Any
du	c_vdT	Any	Ideal gas
dh	c_pdT	Any	Ideal gas

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Compare/Contrast Tables

- For any property relations we have:
  - First law: $Q = \Delta U + W$
  - Work: $W = \int_{path}PdV$
- So what is different?
  - With property tables we use tables to find P-v-T relationships and internal energy
  - Ideal gases use $Pv = RT$ and $du = c_vdT$
    - Use data sources for c_v as average value, c_v as a function of temperature and integrate
    - Find u(T) in ideal gas tables

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Example Calculation

- Given: 10 kg of H_2O at 100 kPa, 200°C expanded to 400°C at constant pressure
- Find: Heat Transfer
  - using H_2O tables (for comparison)
  - using ideal gas with constant heat capacity
  - using ideal gas with variable heat capacity
- First Law: $Q = \Delta U + W = m(u_2 - u_1) + W$
- Path: $W = \int_{path}PdV = P_{1\text{-}2}(V_2 - V_1)$ for constant pressure, $P_{1\text{-}2} = P_1 = P_2$
- $u_2 - u_1 = \int c_vdT$ for ideal gas

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Using H_2O Tables

- At T_1 = 200°C and P_1 = 100 kPa, v_1 = 2.1724 m^3/kg and u_1 = 2658.2 kJ/kg
- At T_2 = 400°C and P_2 = P_1 = 100 kPa, v_2 = 3.1027 m^3/kg and u_2 = 2968.3 kJ/kg
- $W = P_{1\text{-}2}(V_2 - V_1) = P_{1\text{-}2}\, m(v_2 - v_1)$ = (10 kg)(100 kPa)(3.1027 - 2.1724) m^3/kg = 931 kPa·m^3 = 931 kJ
- $Q = m(u_2 - u_1) + W$ = (10 kg)(2968.3 – 2658.2) kJ/kg + 931 kJ = 4,029 kJ

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Ideal Gas Calculations

- $Q = \Delta U + W = m(u_2 - u_1) + \int_{path} PdV$
- $Q = m(u_2 - u_1) + m\int_{path} Pdv$
- $PV = mRT$ $Pv = RT$
- We use $PV = mRT$ to determine mass and specific volume from P and T
- The work calculation does not depend on assumptions about c_v (or $c_p = c_v + R$)
- Find R = 0.4615 kJ/kg·K = 0.4615 kPa·m^3/kg·K in Table A-1, page 908

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Work – Ideal Gas Assumption

- At T_1 = 200°C and P_1 = 100 kPa, $v_1 = RT_1/P_1$ = (.4615 kJ/kg•K)(473.15 K)/(100 kPa) = 2.1836 m^3/kg
- At T_2 = 400°C and P_2 = P_1 = 100 kPa, $v_2 = RT_2/P_2$ = (.4615 kJ/kg•K)(673.15 K)/(100 kPa) = 3.1066 m^3/kg
- $W = P_{1\text{-}2}(V_2 - V_1) = P_{1\text{-}2}\, m(v_2 - v_1)$ = (10 kg)(100 kPa)(3.1066 - 2.1836) m^3/kg = 923 kPa·m^3 = 923 kJ

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Ideal Gas Internal Energy

- $u_2 - u_1 = \int c_v(T)dT = \int c_p(T)dT - R\Delta T$
- Possible calculations for c_v (or c_p)
  - Assume constant (easiest) $\Delta u = c_v\Delta T$ (Table A-2(a), page 909 or Table A-2(b), page 910)
  - Integrate equation for c_v or c_p as a function of temperature (Table A-2(c), p 911)
  - Use ideal gas tables giving u(T) and h(T) (Tables A-17 to A-26, pp 934-947)
  - Last two give molar properties (except air)
    - Divide by molar mass, M, to get per-unit-mass property values

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TABLE A–2

Ideal-gas specific heats of various common gases

(*a*) At 300 K

Gas	Formula	Gas constant, *R* kJ/kg·K	c_p kJ/kg·K	c_v kJ/kg·K
Air	—	0.2870	1.005	0.718
Argon	Ar	0.2081	0.5203	0.3122
Butane	C_4H_{10}	0.1433	1.7164	1.5734
Carbon dioxide	CO_2	0.1889	0.846	0.657
Carbon monoxide	CO	0.2968	1.040	0.744
Ethane	C_2H_6	0.2765	1.7662	1.4897
Ethylene	C_2H_4	0.2964	1.5482	1.2518
Helium	He	2.0769	5.1926	3.1156
Hydrogen	H_2	4.1240	14.307	10.183
Methane	CH_4	0.5182	2.2537	1.7354
Neon	Ne	0.4119	1.0299	0.6179
Nitrogen	N_2	0.2968	1.039	0.743
Octane	C_8H_{18}	0.0729	1.7113	1.6385
Oxygen	O_2	0.2598	0.918	0.658
Propane	C_3H_8	0.1885	1.6794	1.4909
Steam	H_2O	0.4615	1.8723	1.4108

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TABLE A–2

Ideal-gas specific heats of various common gases (*Continued*)

(*b*) At various temperatures

Temperature, K	c_p kJ/kg·K	c_v kJ/kg·K	*k*	c_p kJ/kg·K	c_v kJ/kg·K	*k*
	Air			*Carbon dioxide, CO_2*		
250	1.003	0.716	1.401	0.791	0.602	1.314
300	1.005	0.718	1.400	0.846	0.657	1.288
350	1.008	0.721	1.398	0.895	0.706	1.268
400	1.013	0.726	1.395	0.939	0.750	1.252
450	1.020	0.733	1.391	0.978	0.790	1.239
500	1.029	0.742	1.387	1.014	0.825	1.229
550	1.040	0.753	1.381	1.046	0.857	1.220
600	1.051	0.764	1.376	1.075	0.886	1.213
650	1.063	0.776	1.370	1.102	0.913	1.207

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TABLE A–2

Ideal-gas specific heats of various common gases (*Concluded*)

(*c*) As a function of temperature

$$\bar{c}_p = a + bT + cT^2 + dT^3$$

(T in K, c_p in kJ/kmol·K)

Substance	Formula	*a*	*b*	*c*	*d*
Nitrogen	N_2	28.90	-0.1571×10^{-2}	0.8081×10^{-5}	-2.873×10^{-9}
Oxygen	O_2	25.48	1.520×10^{-2}	-0.7155×10^{-5}	1.312×10^{-9}
Air	—	28.11	0.1967×10^{-2}	0.4802×10^{-5}	-1.966×10^{-9}
Hydrogen	H_2	29.11	-0.1916×10^{-2}	0.4003×10^{-5}	-0.8704×10^{-9}
Carbon monoxide	CO	28.16	0.1675×10^{-2}	0.5372×10^{-5}	-2.222×10^{-9}
Carbon dioxide	CO_2	22.26	5.981×10^{-2}	-3.501×10^{-5}	7.469×10^{-9}
Water vapor	H_2O	32.24	0.1923×10^{-2}	1.055×10^{-5}	-3.595×10^{-9}
Nitric oxide	NO	29.34	-0.09395×10^{-2}	0.9747×10^{-5}	-4.187×10^{-9}

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Constant c_v Ideal Gas

- Get c_v = 1.4108 kJ/kg·K at 300 K (26.85°C) for water from Table A-2(a), p 909 (no data for water in Table A-2(b), page 910)
- $\Delta U = m\Delta u = m \int c_v(T)dT = mc_v(T_2 - T_1) = mc_v\Delta T$, if c_v is constant
- Here, $\Delta U = mc_v(T_2 - T_1)$ = (10 kg) (1.4108 kJ/kg·K)(673.15 K - 473.15 K) = 2,822 kJ
- $Q = \Delta U + W$ = 2,822 kJ + 923 kJ = 3,745 kJ, a 7% error compared to actual properties

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Ideal Gas with $c_v(T)$

$$\Delta\bar{h} = \int_{T_1}^{T_2} \bar{c}_p(T)dT = \int_{T_1}^{T_2} \left(a + bT + cT^2 + dT^3\right)dT$$

$$= a(T_2 - T_1) + \frac{b}{2}\left(T_2^2 - T_1^2\right) + \frac{c}{3}\left(T_2^3 - T_1^3\right) = \frac{d}{4}\left(T_2^4 - T_1^4\right)$$

$$\Delta u = \frac{\Delta\bar{u}}{M} = \frac{\Delta\bar{h} - \bar{R}\Delta T}{M} = \frac{\Delta\bar{h}}{M} - R\Delta T$$

a,b,c,d data from Table A-2(c), page 911
Details not shown here

- Use kelvins for temperature
- Molar enthalpy change = 7229.3 kJ/kmol
- Δu = (7229.3 kJ/kmol) / (18.015 kg/kmol) - (.4615 kJ/kg•K)(200 K) = 309.0 kJ/kg

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Ideal Gas Tables for Water

TABLE A–23

Ideal-gas properties of water vapor, H_2O

T K	$\bar{h}$ kJ/kmol	$\bar{u}$ kJ/kmol	$\bar{s}°$ kJ/kmol·K
0	0	0	0
220	7,295	5,466	178.576
230	7,628	5,715	180.054
240	7,961	5,965	181.471
250	8,294	6,215	182.831
260	8,627	6,466	184.139
270	8,961	6,716	185.399
460	15,428	11,603	203.497
470	15,777	11,869	204.247
480	16,126	12,135	204.982

- T is in kelvins
- Need to interpolate for values at T = 200°C = 473.15 K
- u(200°C) = 11,953 kJ/kmol

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Ideal Gas Tables

- Find molar u(T) for H_2O in Table A-23 on page 946
- Have to interpolate to find the values of u_1 = u(473.15 K) = 11,953 kJ/kmol and u_2 = u(673.15 K) = 17,490 kJ/kmol
- ΔU = (10 kg)(17,490 kJ/kmol - 11,953 kJ/kmol) / (18.015 kg / kmol) = 3,074 kJ
- $Q = \Delta U + W$ = 3,074 kJ + 923 kJ
- Q = 3,997 kJ

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Comparison of Results (kJ)

Method	ΔU	W	Q
Tables	3,098	931	4,029
Const c_v	2,822	923	3,745
$\int c_v(T)dT$	3,090	923	4,013
Ideal gas tables	3,074	923	3,997

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Ideal gases: du = c_vdT

- This does not depend on path
- We just computed the Q = ΔU + W for a constant pressure path of an ideal gas
- We used ΔU = mΔu = m∫c_vdT to compute the internal energy change
- We would use the same equation regardless of the path between state 1 and state 2

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Assuming c_v Constant

- Assumption of constant heat capacity introduces about a 7% error for this problem
- Accounting for temperature variation of heat capacity reduces error to <= 0.8%
- Next page shows figure 4-24, page 177
  - Constant heat capacity assumption is best for noble gases (e.g., argon, neon) and reasonable for diatomic molecules at ambient temperatures
  - Assumption worsens as the temperature range increases

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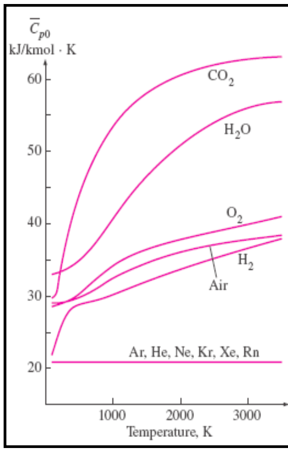

Variation

- Monatomic gases have constant c_p
- Diatomic gases have moderate variation with T
- Triatomic gases have larger variation with T
- What is c_v?

Figure 4-24 from Çengel, *Thermodynamics An Engineering Approach*, 2008

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In-class exercise

- 2 kg of air initially at 100 kPa and 300 K heated to 1200 K. Find the heat transfer for each of the following processes:
  - Constant volume
  - Constant pressure
  - A straight line path to a pressure of 250 kPa
- Use air tables to find the change in internal energy
- How will path affect ΔU?

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In-class Exercise Solution

- Path will ***not*** affect ΔU
  - For an ideal gas, u is a function of temperature only. Since ΔT is the same, ΔU = mΔu will be the same.
  - From air tables, Table A-17, pp 934-935
    - u(300 K) = 214.07 kJ/kg
    - u(1200 K) = 933.33 kJ/kg
    - mΔu = (2 kg)(719.24 kJ/kg) = 1438.48 kJ
  - Q = W + 1438.48 kJ

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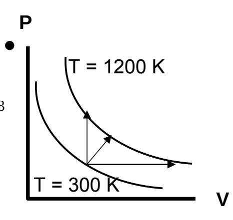
Exercise Solution II

$$V_1 = \frac{mRT_1}{P_1} = \frac{(2\ kg)(300\ K)}{100\ kPa} \frac{0.2870\ kPa \cdot m^3}{kg \cdot K} = 1.722\ m^3$$



- Look at constant volume path first
- For constant volume path, W = 0 so Q = ΔU = 1438.48 kJ

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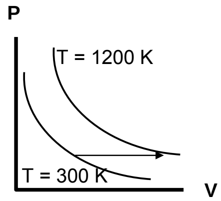
Exercise Solution III

- For constant pressure, $V_2 = V_1(T_2/T_1) = 6.888\ m^3$
- $W = P_{1\text{-}2}(V_2 – V_1) = (100\ kPa)(6.888\ m^3 – 1.722\ m^3) = 516.6\ kJ$



- For constant pressure path, $Q = \Delta U + W = 1438.48\ kJ + 516.66\ kJ = 1955.14\ kJ$

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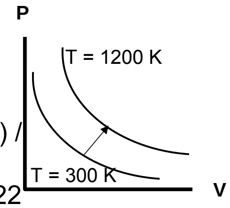
Exercise Solution IV

- For straight line path, $V_2 = V_1(P_1T_2/P_2T_1) = 2.7552\ m^3$
- $W = (P1 + P_2)(V_2 – V_1) / 2 = (100\ kPa + 250\ kPa)(2.7552\ m^3 – 1.722\ m^3) = 180.81\ kJ$



- For this straight-line path, $Q = \Delta U + W = 1438.48\ kJ + 180.81\ kJ = 1619.29\ kJ$

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In-Class Exercise

- Air, initially at 100 psia, 1000 R and 1 ft^3 undergoes an expansion following the polytropic path $PV^{1.3}$ = constant to a final temperature of 500 R. Find the heat transfer.
- For a polytropic path the work is given by the following equation

$$W = \frac{P_2V_2 - P_1V_1}{1-n}$$

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In Class Exercise II

- **Given data:**
  - **Initial state:** $T_1 = 1000$ R, $P_1 = 100$ psia, $V_1 = 1\ ft^3$
  - **Path:** $PV^{1.3}$ = constant
    - $P_1V_1^{1.3} = P_2V_2^{1.3}$
  - **Final state:** $T_2 = 500$ R
  - **Substance:** Air
  - **Property relations:** ideal gas
    - PV = mRT and $du = c_vdT$
    - Air tables give integral of c_vdT

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In Class Exercise III

- **Equations and data:**
  - First Law: $Q = \Delta U + W = m(u_2 – u_1) + W$
  - $W = \int_{path} PdV$
  - $W = (P_2V_2 – P_1V_1) / (1 - n)$ for polytropic path, PV^n = constant
  - PV = mRT
  - $du = c_vdT$ (or use air tables for u, A-17E, pp 982–983 for engineering units)
  - For air, $R = 0.3704\ psia\cdot ft_3/lb_m\cdot R = 0.06855\ Btu/lb_m\cdot R$ (Table A-1E, page 958)

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In Class Exercise IV

- From air tables, $u_1 = u(1000\ R) = 172.43\ Btu/lb_m$ and $u_2 = u(500\ R) = 85.20\ Btu/lb_m$

$$m = \frac{P_1V_1}{RT_1} = \frac{(100\ psia)(1\ ft^3)}{\frac{0.3704\ psia\cdot ft^3}{lb_m\cdot R}(1000\ R)} = 0.2700\ lb_m$$

$$W = \frac{P_2V_2 - P_1V_1}{1-n} = \frac{mRT_2 - mRT_1}{1-n} = \frac{mR(T_2 - T_1)}{1-n}$$

$$= \frac{(0.2700\ lb_m)\frac{0.06855\ Btu}{lb_m\cdot R}(500\ R - 1000\ R)}{1-1.3} = 30.845\ Btu$$

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In Class Exercise V

- $Q = \Delta U + W = m(u_2 - u_1) + W$

$$Q = (0.2700\ lb_m)\left(\frac{85.20\ Btu}{lb_m} - \frac{172.43\ Btu}{lb_m}\right) + 30.845\ Btu$$

Q = 7.29 Btu

- Assuming constant c_v = 0.174 Btu/lb_m·R at mean temperature of 750 R = 290.3°F from Table A-2E(b), page 960 gives Q = 7.36 Btu

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