

Summary of Thermodynamic I

Instructor
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Objectives

- Summarize the following topics
 - ✓ Introduction and Basic Concepts of Thermodynamics
 - ✓ Energy, Energy Transfer, and General Energy Analysis
 - ✓ Properties of Pure Substances
 - ✓ Energy Analysis of Closed Systems
 - ✓ Mass and Energy Analysis of Control Volumes
 - ✓ The Second Law of Thermodynamics
 - ✓ Entropy

Introduction and Basic Concepts of Thermodynamics

- *Thermodynamics* is the science that primarily deals with energy.
- The *first law of thermodynamics* is simply an expression of the «conservation of energy» principle, and it asserts that *energy* is a thermodynamic property.
- The *second law of thermodynamics* asserts that energy has *quality* as well as *quantity*, and actual processes occur in the direction of decreasing quality of energy.
- *Closed system, or Control mass*: A system of fixed mass.
- *Open system, or Control volume*: A system that involves mass transfer across its boundaries.
- *Extensive properties*: The mass-dependent properties of a system.
- *Intensive properties*: Independent of mass properties of a system.
- *Thermodynamic equilibrium*: If a system maintains thermal, mechanical, phase, and chemical equilibrium.

Introduction and Basic Concepts of Thermodynamics

- *Process*: Any change from one state to another.
- *Cycle*: A process with identical end states
- *Quasi-static or Quasi-equilibrium process*: The system remains practically in equilibrium at all times.
- *Zeroth law of thermodynamics*: Two bodies are in thermal equilibrium if both have the same temperature reading even if they are not in contact.

The temperature scales used in the SI and the English system are the *Celsius* scale and the *Fahrenheit* scale, respectively. They are related to absolute temperature scales by

$$T(\text{K}) = T(^{\circ}\text{C}) + 273.15$$

$$T(\text{R}) = T(^{\circ}\text{F}) + 459.67$$

$$\Delta T(\text{K}) = \Delta T(^{\circ}\text{C}) \quad \text{and} \quad \Delta T(\text{R}) = \Delta T(^{\circ}\text{F})$$

Introduction and Basic Concepts of Thermodynamics

The normal force exerted by a fluid per unit area is called *pressure*, and its unit is the *pascal*, $1 \text{ Pa} = 1 \text{ N/m}^2$.

The pressure relative to absolute vacuum is called the *absolute pressure*.

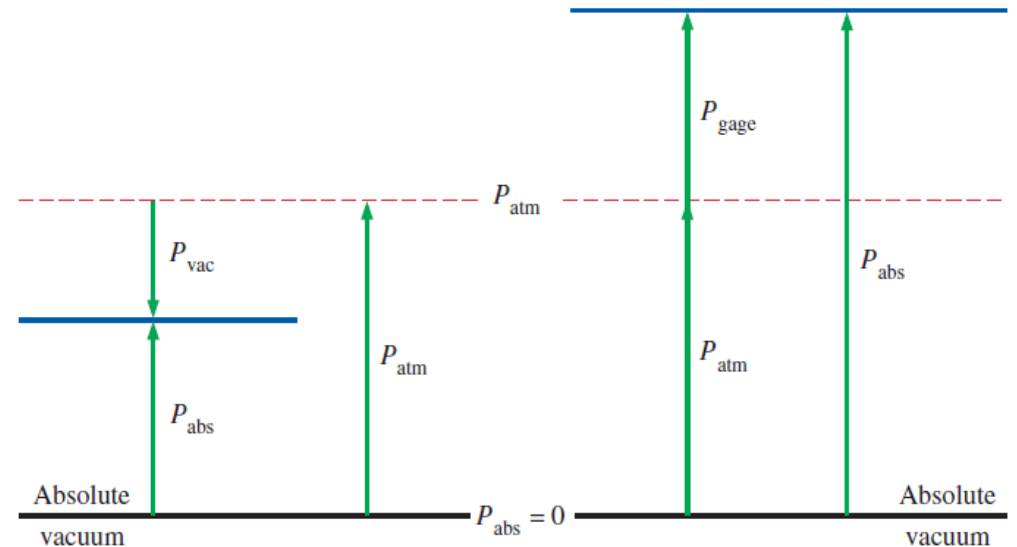
The difference between the absolute pressure and the local atmospheric pressure is called the *gauge pressure*.

Pressures below atmospheric pressure are called *vacuum pressures*.

$$P_{\text{gage}} = P_{\text{abs}} - P_{\text{atm}} \quad (\text{for pressures above } P_{\text{atm}})$$

$$P_{\text{vac}} = P_{\text{atm}} - P_{\text{abs}} \quad (\text{for pressures below } P_{\text{atm}})$$

The pressure at a point in a fluid has the same magnitude in all directions.



Introduction and Basic Concepts of Thermodynamics

The variation of pressure with elevation is given by

$$\frac{dP}{dz} = -\rho g$$

When the density of the fluid is constant, the pressure difference across a fluid layer of thickness Δz is

$$\Delta P = P_2 - P_1 = \rho g \Delta z$$

The absolute and gage pressures in a liquid open to the atmosphere at a depth h from the free surface are

$$P = P_{\text{atm}} + \rho gh \quad \text{or} \quad P_{\text{gage}} = \rho gh$$

Introduction and Basic Concepts of Thermodynamics

- Small to moderate pressure differences are measured by a *manometer*.
- The pressure in a stationary fluid remains constant in the horizontal direction.
- **Pascal's principle**: The pressure applied to a confined fluid increases the pressure throughout by the same amount.
- The atmospheric pressure is measured by a *barometer* and is given by

$$P_{\text{atm}} = \rho gh$$

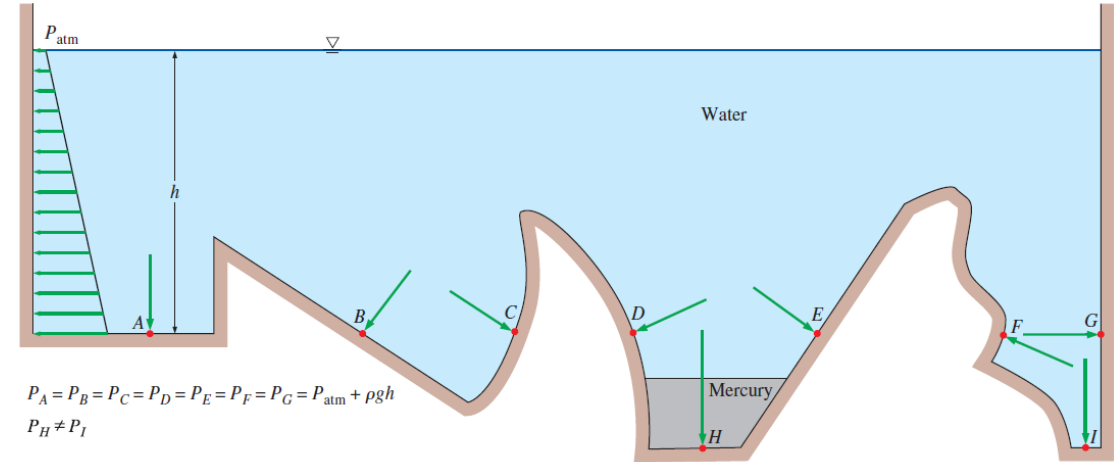
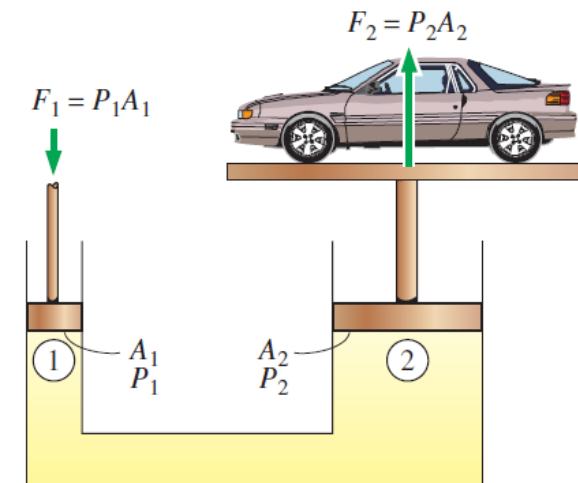


FIGURE 1-46

Under hydrostatic conditions, the pressure is the same at all points on a horizontal plane in a given fluid regardless of geometry, provided that the points are interconnected by the same fluid.



Energy, Energy Transfer, and General Energy Analysis

- *Total energy*: The sum of all forms of energy of a system (internal, kinetic and potential)
- *Internal energy*: The molecular energy of a system and may exist in sensible, latent, chemical, and nuclear forms.
- *Mass flow rate, $\dot{m}$* : The amount of mass flowing through a cross section per unit time.

$$\dot{m} = \rho \dot{V} = \rho A_c V_{\text{avg}}$$

The energy flow rate associated with a fluid flowing at a rate of $\dot{m}$ is

$$\dot{E} = \dot{m}e$$

Energy, Energy Transfer, and General Energy Analysis

The *mechanical energy* is defined as the form of energy that can be converted to mechanical work completely and directly by a mechanical device such as an ideal turbine.

$$e_{\text{mech}} = \frac{P}{\rho} + \frac{V^2}{2} + gz$$

$$\dot{E}_{\text{mech}} = \dot{m}e_{\text{mech}} = \dot{m}\left(\frac{P}{\rho} + \frac{V^2}{2} + gz\right)$$

where P/ρ is the *flow energy*, $V^2/2$ is the *kinetic energy*, and gz is the *potential energy* of the fluid per unit mass.

Energy can cross the boundaries of a closed system in the form of *heat* or *work*. For control volumes, energy can also be transported by *mass*. If the energy transfer is due to a temperature difference between a closed system and its surroundings, it is *heat*; otherwise, it is *work*.

Energy, Energy Transfer, and General Energy Analysis

Various forms of work are expressed as follows:

$$\text{Electrical work: } W_e = \mathbf{VI}\Delta t$$

$$\text{Shaft work: } W_{\text{sh}} = 2\pi nT$$

$$\text{Spring work: } W_{\text{spring}} = \frac{1}{2}k(x_2^2 - x_1^2)$$

First law of thermodynamics: An expression of the conservation of energy principle, also called the *energy balance*. The general mass and energy balances for *any system* undergoing *any process* can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{\Delta E_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}} \quad (\text{kJ})$$

$$\underbrace{\dot{E}_{\text{in}} - \dot{E}_{\text{out}}}_{\text{Rate of net energy transfer by heat, work, and mass}} = \underbrace{dE_{\text{system}}/dt}_{\text{Rate of change in internal, kinetic, potential, etc., energies}} \quad (\text{kW})$$

Energy, Energy Transfer, and General Energy Analysis

The efficiencies of various devices are defined as

$$\eta_{\text{pump}} = \frac{\Delta \dot{E}_{\text{mech, fluid}}}{\dot{W}_{\text{shaft, in}}} = \frac{\dot{W}_{\text{pump, u}}}{\dot{W}_{\text{pump}}}$$

$$\eta_{\text{turbine}} = \frac{\dot{W}_{\text{shaft, out}}}{|\Delta \dot{E}_{\text{mech, fluid}}|} = \frac{\dot{W}_{\text{turbine}}}{\dot{W}_{\text{turbine, e}}}$$

$$\eta_{\text{motor}} = \frac{\text{Mechanical power output}}{\text{Electric power input}} = \frac{\dot{W}_{\text{shaft, out}}}{\dot{W}_{\text{elect, in}}}$$

$$\eta_{\text{generator}} = \frac{\text{Electric power output}}{\text{Mechanical power input}} = \frac{\dot{W}_{\text{elect, out}}}{\dot{W}_{\text{shaft, in}}}$$

$$\text{Efficiency} = \frac{\text{Desired output}}{\text{Required input}}$$

$$\eta_{\text{turbine-gen}} = \eta_{\text{turbine}} \eta_{\text{generator}} = \frac{\dot{W}_{\text{elect, out}}}{|\Delta \dot{E}_{\text{mech, fluid}}|}$$

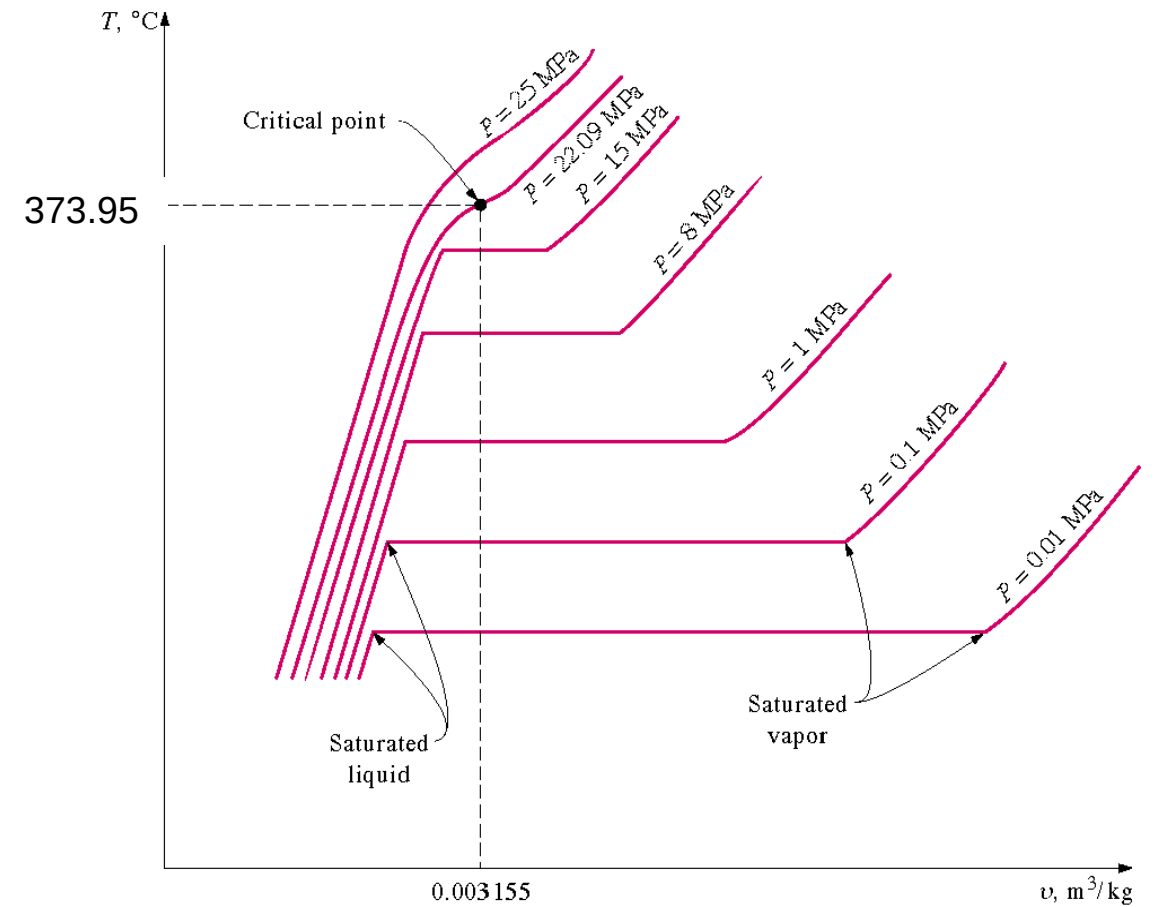
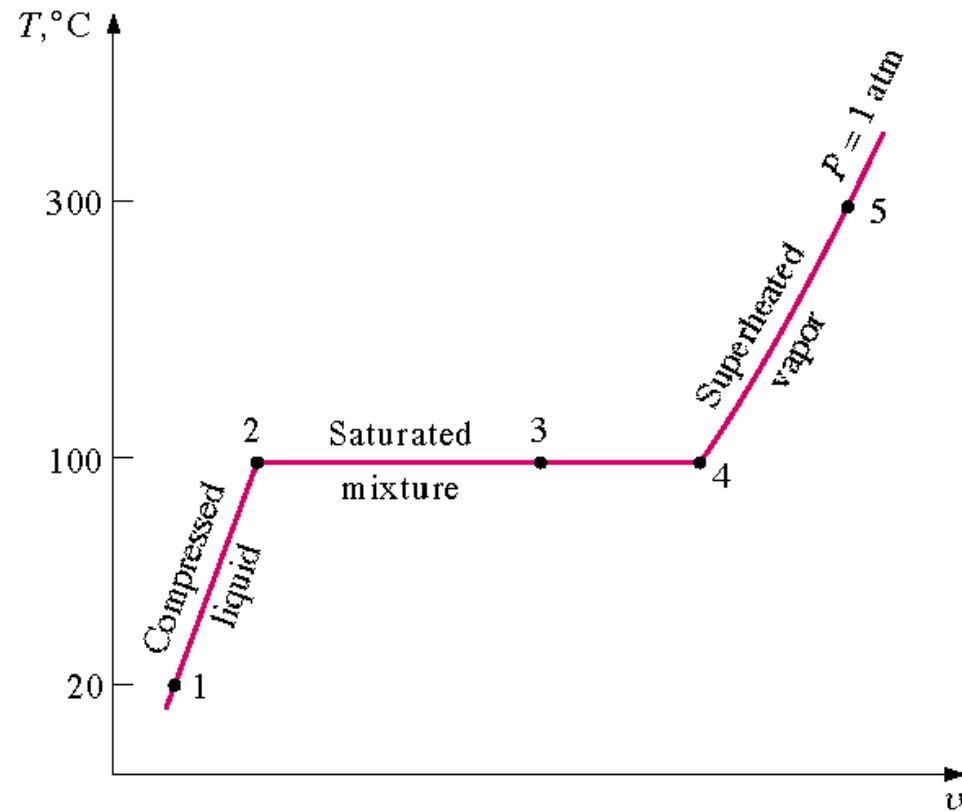
$$\eta_{\text{pump-motor}} = \eta_{\text{pump}} \eta_{\text{motor}} = \frac{\Delta \dot{E}_{\text{mech, fluid}}}{\dot{W}_{\text{elect, in}}}$$

The conversion of energy from one form to another is often associated with adverse effects on the environment, and environmental impact should be an important consideration in the conversion and utilization of energy.

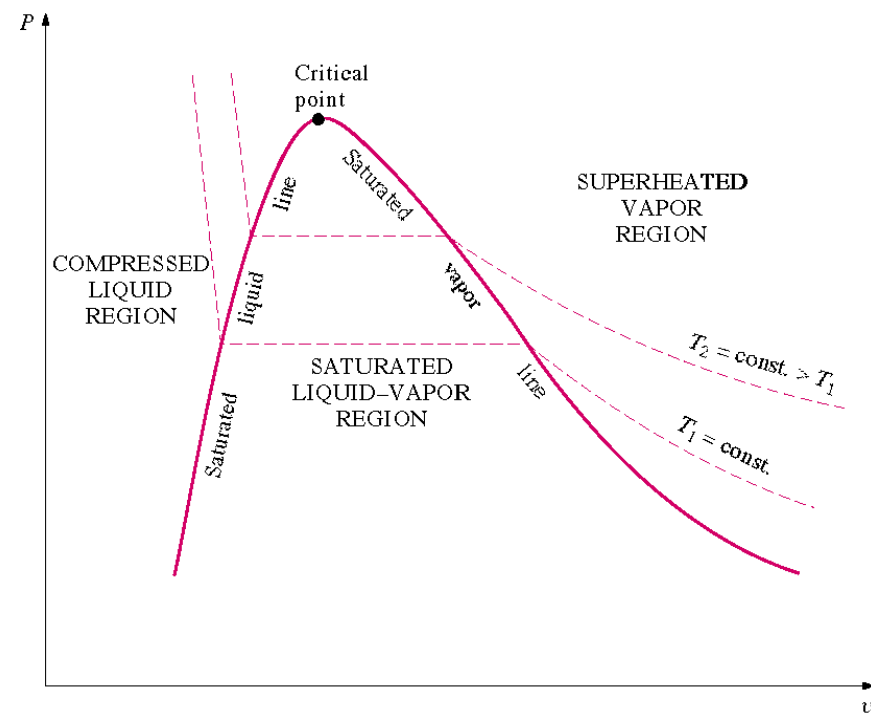
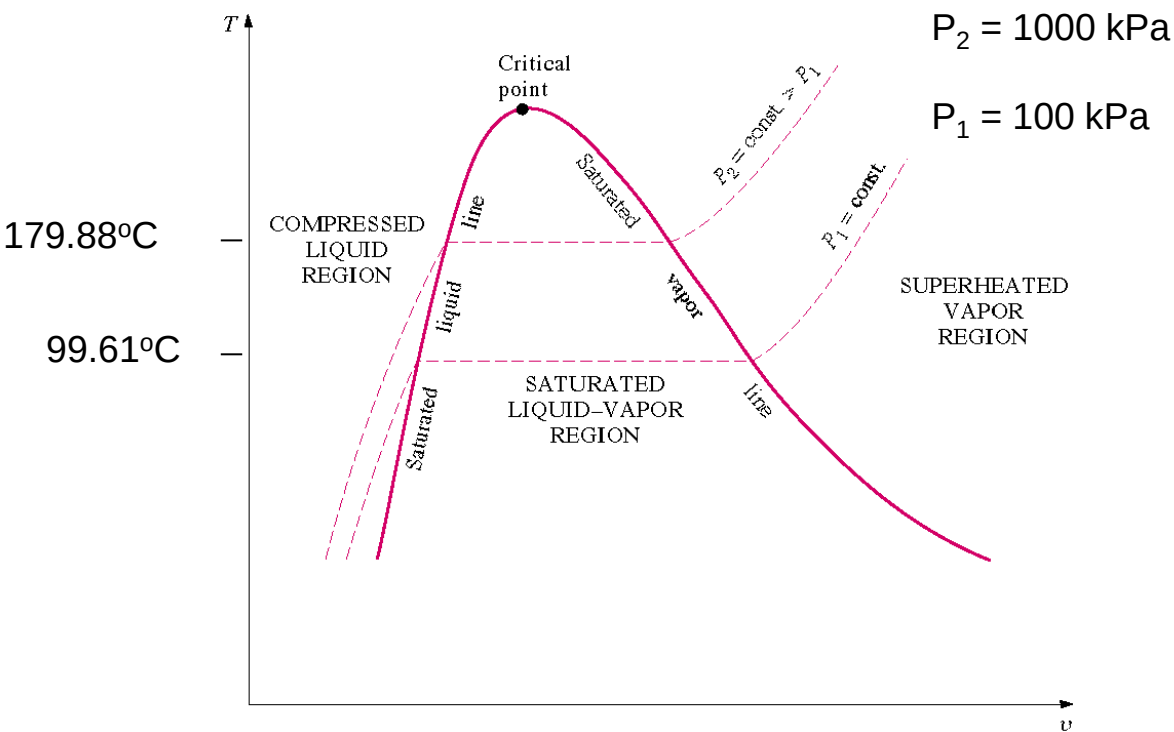
Properties of Pure Substances

- *Pure substance*: A substance that has a fixed chemical composition throughout.
- Depending on its energy level a substance can be in different phases.
- *Compressed or subcooled liquid*: A substance that is not about to vaporize is in the liquid form.
- *Superheated vapor*: A substance that is not about to condense is in the gas phase.
- *Saturation temperature*: At a given pressure, the temperature at which a substance changes phase.
- *Saturation pressure*: At a given temperature, the pressure at which a substance changes phase.
- *Saturated liquid and Saturated vapor*: During a boiling process, both the liquid and the vapor phases coexist in equilibrium, and under this condition the liquid is called *saturated liquid* and the vapor *saturated vapor*.

Properties of Pure Substances



Properties of Pure Substances



Properties of Pure Substances

Quality: In a saturated liquid–vapor mixture, the mass fraction of vapor.

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}} \quad x = \frac{\text{mass}_{\text{saturated vapor}}}{\text{mass}_{\text{total}}} = \frac{m_g}{m_f + m_g}$$

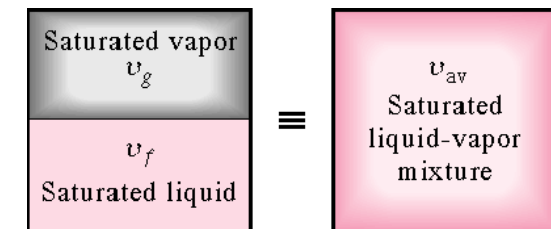
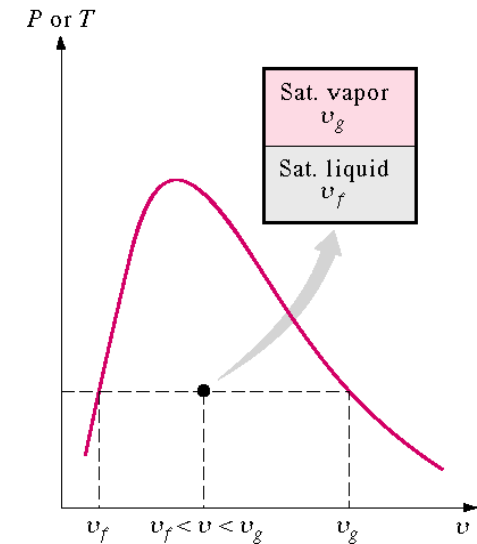
Quality may have values between 0 (saturated liquid) and 1 (saturated vapor). The average value of any intensive property «y» is determined from

$$y = y_f + xy_{fg}$$

In the absence of compressed liquid data, a general approximation is to treat a compressed liquid as a saturated liquid at the given temperature,

$$y \cong y_{f@T}$$

$$h \cong h_{f@T} + v_f (P - P_{\text{sat}})$$



Saturated Water-
Temperature Table

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}}$$

$$y = y_f + xy_{fg}$$

where y stands for v, u, or h.

Temp., T °C	Sat. Press., P _{sat} kPa	Specific volume, m³/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg·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	0.00	2374.9	2374.9	0.00	2500.9	2500.9	0.0000	9.1556	9.1556
5	0.8725	0.001000	147.03	21.02	2360.8	2381.8	21.02	2489.1	2510.1	0.0763	8.9487	9.0249
10	1.228	0.001000	106.32	42.02	2346.6	2388.7	42.02	2477.2	2519.2	0.1511	8.7488	8.8999
15	1.706	0.001001	77.885	62.98	2332.5	2395.5	62.98	2465.4	2528.3	0.2245	8.5559	8.7803
20	2.339	0.001002	57.762	83.91	2318.4	2402.3	83.91	2453.5	2537.4	0.2965	8.3696	8.6661
25	3.170	0.001003	43.340	104.83	2304.3	2409.1	104.83	2441.7	2546.5	0.3672	8.1895	8.5567
30	4.247	0.001004	32.879	125.73	2290.2	2415.9	125.74	2429.8	2555.6	0.4368	8.0152	8.4520
35	5.629	0.001006	25.205	146.63	2276.0	2422.7	146.64	2417.9	2564.6	0.5051	7.8466	8.3517
40	7.385	0.001008	19.515	167.53	2261.9	2429.4	167.53	2406.0	2573.5	0.5724	7.6832	8.2556
45	9.595	0.001010	15.251	188.43	2247.7	2436.1	188.44	2394.0	2582.4	0.6386	7.5247	8.1633
50	12.35	0.001012	12.026	209.33	2233.4	2442.7	209.34	2382.0	2591.3	0.7038	7.3710	8.0748
55	15.76	0.001015	9.5639	230.24	2219.1	2449.3	230.26	2369.8	2600.1	0.7680	7.2218	7.9898
60	19.95	0.001017	7.6670	251.16	2204.7	2455.9	251.18	2357.7	2608.8	0.8313	7.0769	7.9082
65	25.04	0.001020	6.1935	272.09	2190.3	2462.4	272.12	2345.4	2617.5	0.8937	6.9360	7.8296
70	31.20	0.001023	5.0396	293.04	2175.8	2468.9	293.07	2333.0	2626.1	0.9551	6.7989	7.7540
75	38.60	0.001026	4.1291	313.99	2161.3	2475.3	314.03	2320.6	2634.6	1.0158	6.6655	7.6812
80	47.42	0.001029	3.4053	334.97	2146.6	2481.6	335.02	2308.0	2643.0	1.0756	6.5355	7.6111
85	57.87	0.001032	2.8261	355.96	2131.9	2487.8	356.02	2295.3	2651.4	1.1346	6.4089	7.5435
90	70.18	0.001036	2.3593	376.97	2117.0	2494.0	377.04	2282.5	2659.6	1.1929	6.2853	7.4782
95	84.61	0.001040	1.9808	398.00	2102.0	2500.1	398.09	2269.6	2667.6	1.2504	6.1647	7.4151
100	101.42	0.001043	1.6720	419.06	2087.0	2506.0	419.17	2256.4	2675.6	1.3072	6.0470	7.3542
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360	18666	0.001895	0.006950	1726.16	625.7	2351.9	1761.53	720.1	2481.6	3.9165	1.1373	5.0537
365	19822	0.002015	0.006009	1777.22	526.4	2303.6	1817.16	605.5	2422.7	4.0004	0.9489	4.9493
370	21044	0.002217	0.004953	1844.53	385.6	2230.1	1891.19	443.1	2334.3	4.1119	0.6890	4.8009
373.95	22064	0.003106	0.003106	2015.8	0	2015.8	2084.3	0	2084.3	4.4070	0	4.4070

Saturated Water -
Pressure Table

$$x = \frac{m_{\text{vapor}}}{m_{\text{total}}}$$

$$y = y_f + xy_{fg}$$

where y stands for v , u , or h .

Press. P kPa	Sat. Temp., T_{sat} °C	Specific volume, m^3/kg			Internal energy, kJ/kg		Enthalpy, kJ/kg			Entropy, kJ/kg·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
0.6117	0.01	0.001000	206.00	0.00	2374.9	2374.9	0.00	2500.9	2500.9	0.0000	9.1556	9.1556
1.0	6.97	0.001000	129.19	29.30	2355.2	2384.5	29.30	2484.4	2513.7	0.1059	8.8690	8.9749
1.5	13.02	0.001001	87.964	54.69	2338.1	2392.8	54.69	2470.1	2524.7	0.1956	8.6314	8.8270
2.0	17.50	0.001001	66.990	73.43	2325.5	2398.9	73.43	2459.5	2532.9	0.2606	8.4621	8.7227
2.5	21.08	0.001002	54.242	88.42	2315.4	2403.8	88.42	2451.0	2539.4	0.3118	8.3302	8.6421
3.0	24.08	0.001003	45.654	100.98	2306.9	2407.9	100.98	2443.9	2544.8	0.3543	8.2222	8.5765
4.0	28.96	0.001004	34.791	121.39	2293.1	2414.5	121.39	2432.3	2553.7	0.4224	8.0510	8.4734
5.0	32.87	0.001005	28.185	137.75	2282.1	2419.8	137.75	2423.0	2560.7	0.4762	7.9176	8.3938
7.5	40.29	0.001008	19.233	168.74	2261.1	2429.8	168.75	2405.3	2574.0	0.5763	7.6738	8.2501
10	45.81	0.001010	14.670	191.79	2245.4	2437.2	191.81	2392.1	2583.9	0.6492	7.4996	8.1488
15	53.97	0.001014	10.020	225.93	2222.1	2448.0	225.94	2372.3	2598.3	0.7549	7.2522	8.0071
20	60.06	0.001017	7.6481	251.40	2204.6	2456.0	251.42	2357.5	2608.9	0.8320	7.0752	7.9073
25	64.96	0.001020	6.2034	271.93	2190.4	2462.4	271.96	2345.5	2617.5	0.8932	6.9370	7.8302
30	69.09	0.001022	5.2287	289.24	2178.5	2467.7	289.27	2335.3	2624.6	0.9441	6.8234	7.7675
40	75.86	0.001026	3.9933	317.58	2158.8	2476.3	317.62	2318.4	2636.1	1.0261	6.6430	7.6691
50	81.32	0.001030	3.2403	340.49	2142.7	2483.2	340.54	2304.7	2645.2	1.0912	6.5019	7.5931
75	91.76	0.001037	2.2172	384.36	2111.8	2496.1	384.44	2278.0	2662.4	1.2132	6.2426	7.4558
100	99.61	0.001043	1.6941	417.40	2088.2	2505.6	417.51	2257.5	2675.0	1.3028	6.0562	7.3589
125	105.97	0.001048	1.3750	444.23	2068.8	2513.0	444.36	2240.6	2684.9	1.3741	5.9100	7.2841
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
20,000	365.75	0.002038	0.005862	1785.84	509.0	2294.8	1826.59	585.5	2412.1	4.0146	0.9164	4.9310
21,000	369.83	0.002207	0.004994	1841.62	391.9	2233.5	1887.97	450.4	2338.4	4.1071	0.7005	4.8076
22,000	373.71	0.002703	0.003644	1951.65	140.8	2092.4	2011.12	161.5	2172.6	4.2942	0.2496	4.5439
22,064	373.95	0.003106	0.003106	2015.8	0	2015.8	2084.3	0	2084.3	4.4070	0	4.4070

Superheated Water Table

TABLE A-6 Superheated water

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K
$P = 0.01 \text{ MPa (45.81°C)}$				
Sat.	14.670	2437.2	2583.9	8.1488
50	14.867	2443.3	2592.0	8.1741
100	17.196	2515.5	2687.5	8.4489
150	19.513	2587.9	2783.0	8.6893
200	21.826	2661.4	2879.6	8.9049
250	24.136	2736.1	2977.5	9.1015
300	26.446	2812.3	3076.7	9.2827
400	31.063	2969.3	3280.0	9.6094
500	35.680	3132.9	3489.7	9.8998
600	40.296	3303.3	3706.3	10.1631
700	44.911	3480.8	3929.9	10.4056
800	49.527	3665.4	4160.6	10.6312
900	54.143	3856.9	4398.3	10.8429
1000	58.758	4055.3	4642.8	11.0429
1100	63.373	4260.0	4893.8	11.2326
1200	67.989	4470.9	5150.8	11.4132
1300	72.604	4687.4	5413.4	11.5857

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K
$P = 0.05 \text{ MPa (81.32°C)}$				
Sat.	3.2403	2483.2	2645.2	7.5931
100	3.4187	2511.5	2682.4	7.6953
150	3.8897	2585.7	2780.2	7.9413
200	4.3562	2660.0	2877.8	8.1592
250	4.8206	2735.1	2976.2	8.3568
300	5.2841	2811.6	3075.8	8.5387
400	6.2094	2968.9	3279.3	8.8659
500	7.1338	3132.6	3489.3	9.1566
600	8.0577	3303.1	3706.0	9.4201
700	8.9813	3480.6	3929.7	9.6626
800	9.9047	3665.2	4160.4	9.8883
900	10.828	3856.8	4398.2	10.1000
1000	11.751	4055.2	4642.7	10.3000
1100	12.675	4259.9	4893.7	10.4897
1200	13.598	4470.8	5150.7	10.6704
1300	14.521	4687.3	5413.3	10.8429

Compressed Liquid Water Table

TABLE A-7 Compressed liquid water

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K
$P = 5 \text{ MPa (263.94°C)}$				
Sat.	0.0012862	1148.1	1154.5	2.9207
0	0.0009977	0.04	5.03	0.0001
20	0.0009996	83.61	88.61	0.2954
40	0.0010057	166.92	171.95	0.5705
60	0.0010149	250.29	255.36	0.8287
80	0.0010267	333.82	338.96	1.0723
100	0.0010410	417.65	422.85	1.3034
120	0.0010576	501.91	507.19	1.5236
140	0.0010769	586.80	592.18	1.7344
160	0.0010988	672.55	678.04	1.9374
180	0.0011240	759.47	765.09	2.1338
200	0.0011531	847.92	853.68	2.3251
220	0.0011868	938.39	944.32	2.5127
240	0.0012268	1031.6	1037.7	2.6983
260	0.0012755	1128.5	1134.9	2.8841

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K
$P = 10 \text{ MPa (311.00°C)}$				
Sat.	0.0014522	1393.3	1407.9	3.3603
0	0.0009952	0.12	10.07	0.0003
20	0.0009973	83.31	93.28	0.2943
40	0.0010035	166.33	176.37	0.5685
60	0.0010127	249.43	259.55	0.8260
80	0.0010244	332.69	342.94	1.0691
100	0.0010385	416.23	426.62	1.2996
120	0.0010549	500.18	510.73	1.5191
140	0.0010738	584.72	595.45	1.7293
160	0.0010954	670.06	681.01	1.9316
180	0.0011200	756.48	767.68	2.1271
200	0.0011482	844.32	855.80	2.3174
220	0.0011809	934.01	945.82	2.5037
240	0.0012192	1026.2	1038.3	2.6876
260	0.0012653	1121.6	1134.3	2.8710
280	0.0013226	1221.8	1235.0	3.0565
300	0.0013980	1329.4	1343.3	3.2488

TABLE A-8
Saturated ice-water vapor

Temp., T °C	Sat. Press., P_{sat} kPa	Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg			Entropy, kJ/kg·K		
		Sat. ice, v_i	Sat. vapor, v_g	Sat. ice, u_i	Subl., u_{ig}	Sat. vapor, u_g	Sat. ice, h_i	Subl., h_{ig}	Sat. vapor, h_g	Sat. ice, s_i	Subl., s_{ig}	Sat. vapor, s_g
0.01	0.6117	0.0010909	206.0	-333.40		2374.5	-333.40		2500.5	-1.220		9.154
0	0.6112	0.0010909	206.2	-333.43	2707.9	2374.5	-333.43	2833.9	2500.5	-1.220	10.375	9.154
-2	0.5177	0.0010905	241.6	-337.63	2709.4	2371.8	-337.63	2834.5	2496.8	-1.236	10.453	9.218
-4	0.4375	0.0010902	283.8	-341.80	2710.8	2369.0	-341.80	2835.0	2493.2	-1.251	10.533	9.282
-6	0.3687	0.0010898	334.3	-345.94	2712.2	2366.2	-345.93	2835.4	2489.5	-1.267	10.613	9.347
-8	0.3100	0.0010895	394.7	-350.04	2713.5	2363.5	-350.04	2835.8	2485.8	-1.282	10.695	9.413
-10	0.2599	0.0010892	467.2	-354.12	2714.8	2360.7	-354.12	2836.2	2482.1	-1.298	10.778	9.480
.	.	.	.	.	.	.	.	.	.	.	.	.
.	.	.	.	.	.	.	.	.	.	.	.	.
-36	0.0200	0.0010850	5460.1	-404.40	2729.0	2324.6	-404.40	2838.4	2434.0	-1.499	11.969	10.470
-38	0.0161	0.0010847	6750.5	-408.07	2729.9	2321.8	-408.07	2838.4	2430.3	-1.514	12.071	10.557
-40	0.0128	0.0010844	8376.7	-411.70	2730.7	2319.0	-411.70	2838.3	2426.6	-1.530	12.174	10.644

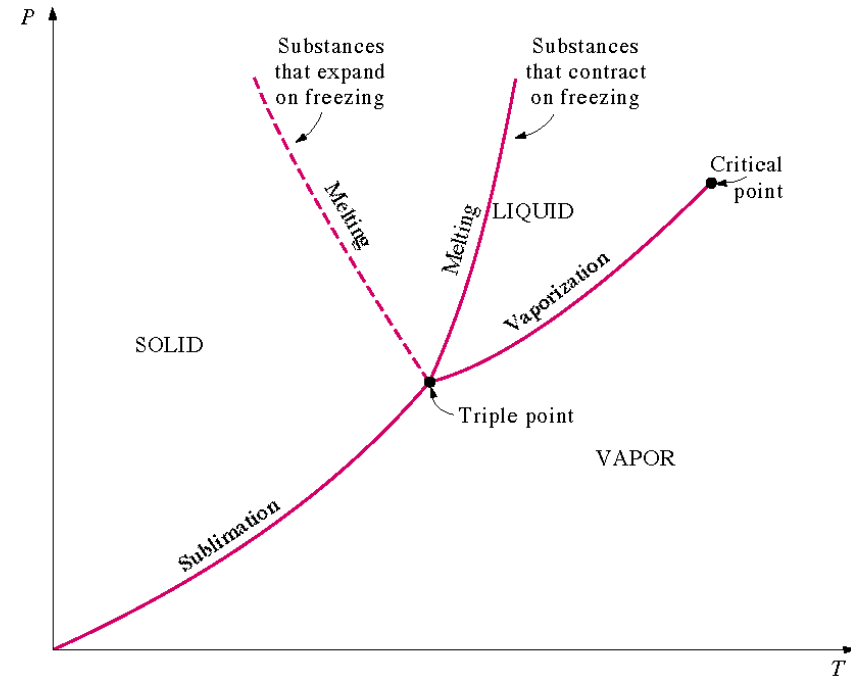
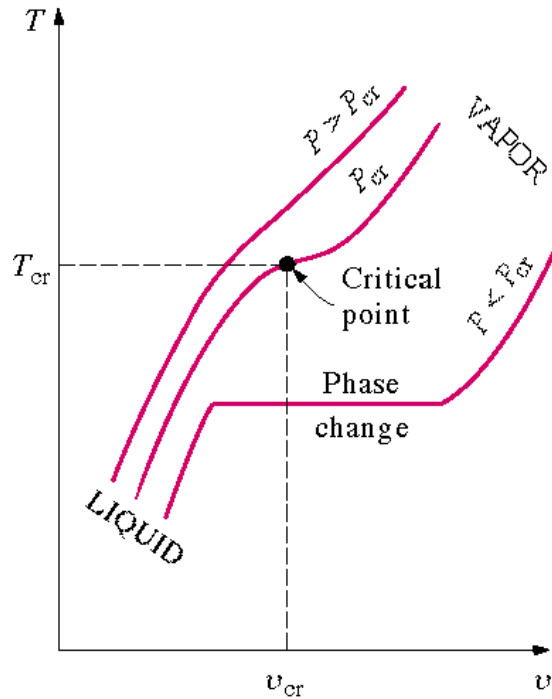
Properties of Pure Substances

- *Critical point*: The point at which the saturated liquid and saturated vapor states are identical. At pressures above the critical pressure, there is not a distinct phasechange process. The temperature, pressure, and specific volume of a substance at the critical point are called, respectively, the *critical temperature* T_{cr} , *critical pressure* P_{cr} , and *critical specific volume* v_{cr} .
- *Triple line*: All three phases of a substance coexist in equilibrium at states along.
- *Equation of state*: Any relation among the pressure, temperature, and specific volume of a substance.
- The simplest and best-known equation of state is the *ideal gas equation of state*, given as

$$Pv = RT$$

where R is the gas constant.

Properties of Pure Substances



The triple point of water is 0.01 °C, 0.6117 kPa (See Table 3-3).

The critical point of water is 373.95 °C, 22.064 MPa (See Table A-1).

Properties of Pure Substances

- Real gases exhibit ideal-gas behavior at relatively low pressures and high temperatures. An ideal gas is a fictitious substance.
- The deviation from ideal-gas behavior can be properly accounted for by using the *compressibility factor Z*, defined as

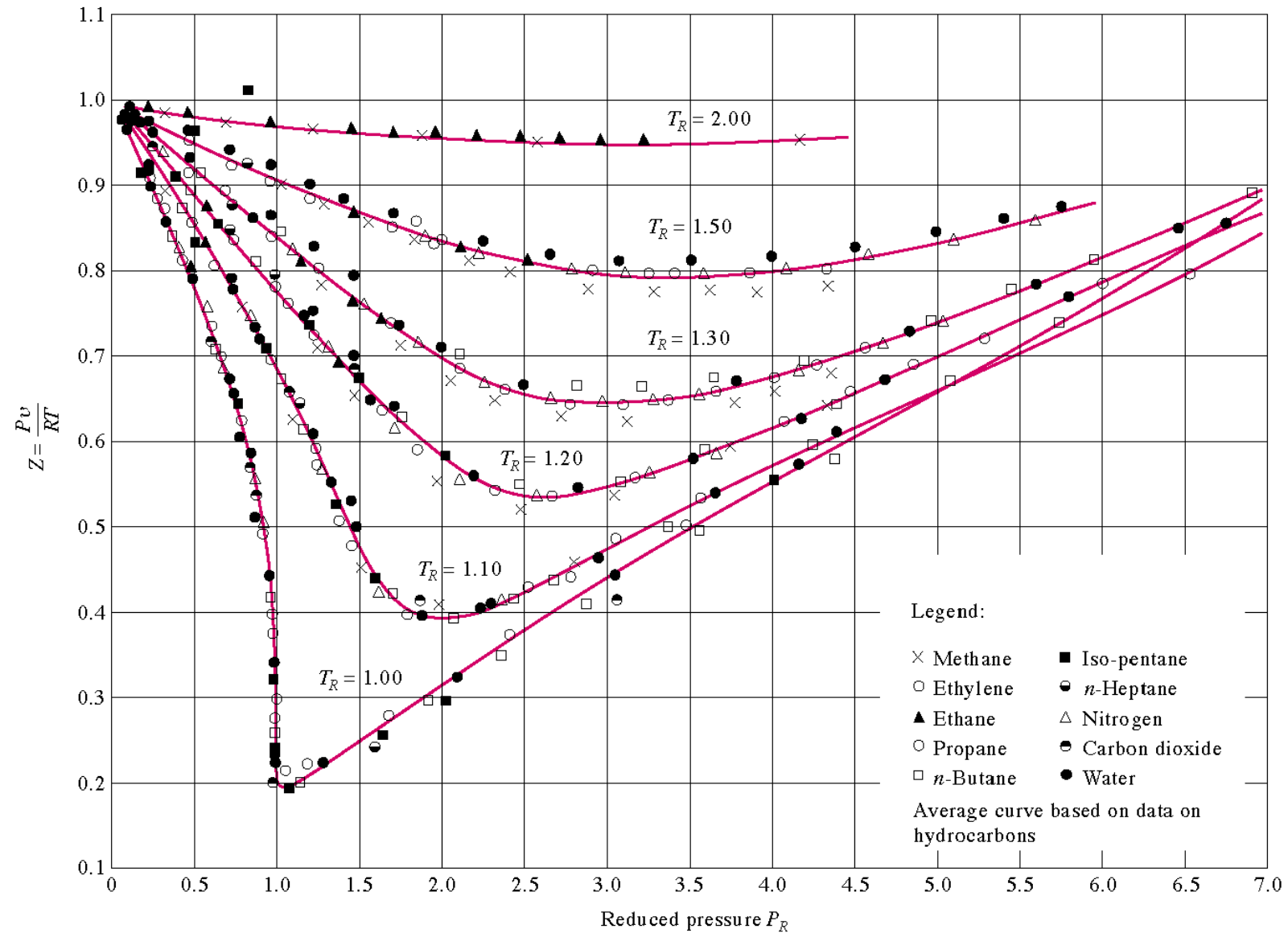
$$Z = \frac{Pv}{RT} \quad \text{or} \quad Z = \frac{v_{\text{actual}}}{v_{\text{ideal}}}$$

- The Z factor is approximately the same for all gases at the same *reduced temperature* and *reduced pressure*, which are defined as

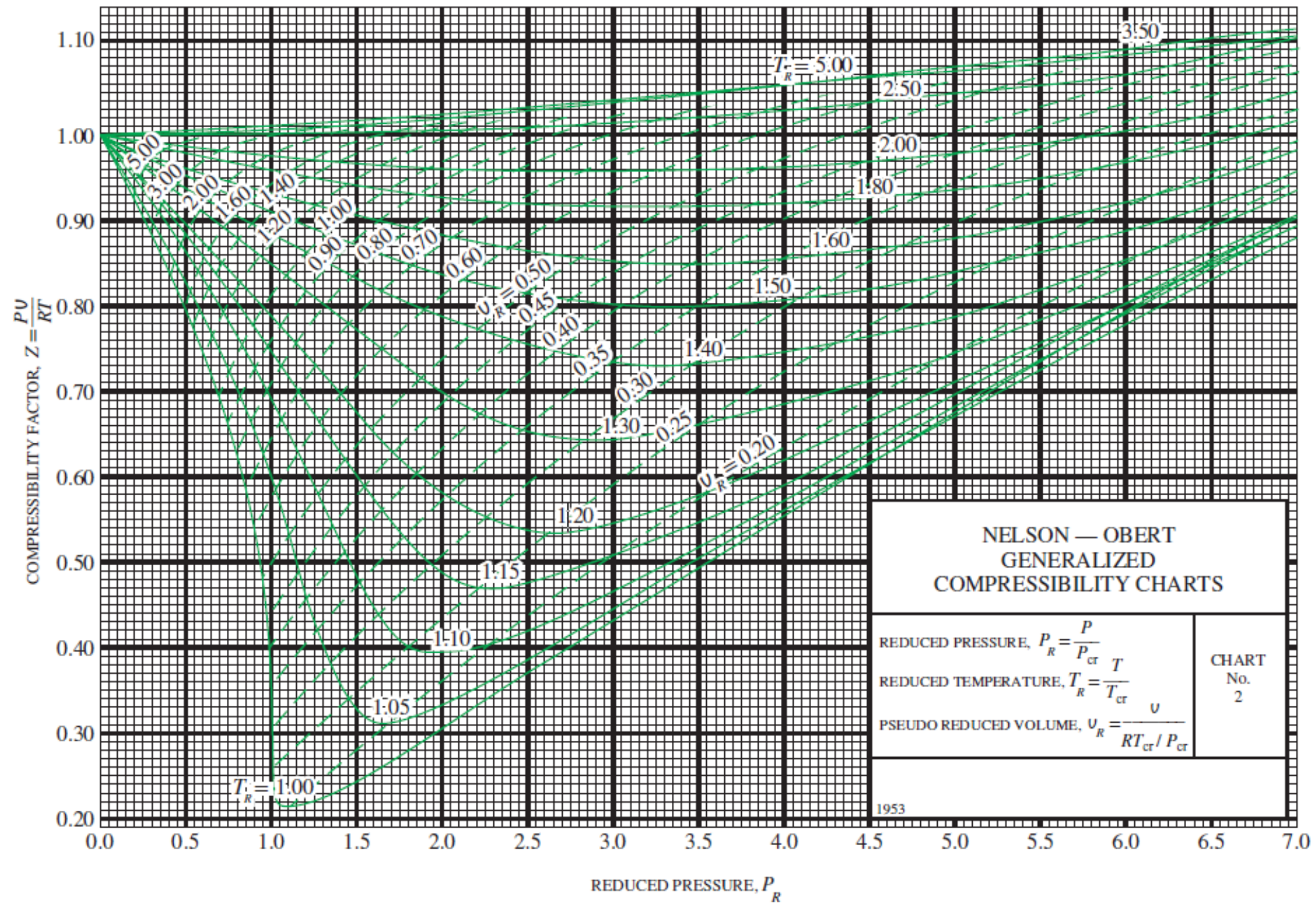
$$T_R = \frac{T}{T_{\text{cr}}} \quad \text{and} \quad P_R = \frac{P}{P_{\text{cr}}}$$

- where P_{cr} and T_{cr} are the critical pressure and temperature, respectively. This is known as the *principle of corresponding states*.

Properties of Pure Substances



(b) Intermediate pressures, $0 < P_R < 7$



Properties of Pure Substances

- When either P or T is unknown, it can be determined from the compressibility chart with the help of the *pseudo-reduced specific volume*, defined as

$$v_R = \frac{v_{\text{actual}}}{RT_{\text{cr}}/P_{\text{cr}}}$$

- The P-v-T behavior of substances can be represented more accurately by more complex equations of state. Three of the best known are

$$\text{van der Waals: } \left(P + \frac{a}{v^2} \right) (v - b) = RT$$

$$a = \frac{27R^2T_{\text{cr}}^2}{64P_{\text{cr}}} \quad \text{and} \quad b = \frac{RT_{\text{cr}}}{8P_{\text{cr}}}$$

Properties of Pure Substances

$$\text{Beattie-Bridgeman: } P = \frac{R_u T}{\bar{v}^2} \left(1 - \frac{c}{\bar{v} T^3} \right) (\bar{v} + B) - \frac{A}{\bar{v}^2}$$

$$A = A_0 \left(1 - \frac{a}{\bar{v}} \right) \quad \text{and} \quad B = B_0 \left(1 - \frac{b}{\bar{v}} \right)$$

Benedict-Webb-Rubin:

$$P = \frac{R_u T}{\bar{v}} + \left(B_0 R_u T - A_0 - \frac{C_0}{T^2} \right) \frac{1}{\bar{v}^2} + \frac{b R_u T - a}{\bar{v}^3} + \frac{a \alpha}{\bar{v}^6} \\ + \frac{c}{\bar{v}^3 T^2} \left(1 + \frac{\gamma}{\bar{v}^2} \right) e^{-\gamma/\bar{v}^2}$$

where R_u is the universal gas constant and $\bar{v}$ is the molar specific volume.

Energy Analysis of Closed Systems

- Work is the energy transferred as a force acts on a system through a distance.
- *Boundary work*: The work associated with the expansion and compression of substances. On a P-V diagram, the area under the process curve represents the boundary work for a quasi-equilibrium process. Various forms of boundary work are expressed as follows:

General

$$W_b = \int_1^2 P dV$$

Isobaric process

$$W_b = P_0(V_2 - V_1) \quad (P_1 = P_2 = P_0 = \text{constant})$$

Polytropic process

$$W_b = \frac{P_2 V_2 - P_1 V_1}{1 - n} \quad (n \neq 1) \quad (PV^n = \text{constant})$$

Isothermal process
of an ideal gas

$$W_b = P_1 V_1 \ln \frac{V_2}{V_1} = mRT_0 \ln \frac{V_2}{V_1} \quad (PV = mRT_0 = \text{constant})$$

Energy Analysis of Closed Systems

- The general energy balances for *any system* undergoing *any process* can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{\Delta E_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}}$$

$$\underbrace{\dot{E}_{\text{in}} - \dot{E}_{\text{out}}}_{\text{Rate of net energy transfer by heat, work, and mass}} = \underbrace{dE_{\text{system}}/dt}_{\text{Rate of change in internal, kinetic, potential, etc., energies}}$$

- Taking heat transfer *to* the system and work done *by* the system to be *positive quantities*, the energy balance for a closed system can also be expressed as

$$Q - W = \Delta U + \Delta \text{KE} + \Delta \text{PE}$$

$$\left\{ \begin{array}{l} W = W_{\text{other}} + W_b \\ \Delta U = m(u_2 - u_1) \\ \Delta \text{KE} = \frac{1}{2}m(V_2^2 - V_1^2) \\ \Delta \text{PE} = mg(z_2 - z_1) \end{array} \right.$$

Energy Analysis of Closed Systems

- For a *constant-pressure process*,

$$W_b + \Delta U = \Delta H \quad \longrightarrow \quad Q - W_{\text{other}} = \Delta H + \Delta \text{KE} + \Delta \text{PE}$$

- The amount of energy needed to raise the temperature of a unit mass of a substance by one degree is called the *specific heat at constant volume* c_v for a constant-volume process and the *specific heat at constant-pressure* c_p for a constant pressure process. They are defined as

$$c_v = \left(\frac{\partial u}{\partial T} \right)_v \quad \text{and} \quad c_p = \left(\frac{\partial h}{\partial T} \right)_p$$

Energy Analysis of Closed Systems

- For ideal gases u , h , c_v , and c_p are functions of temperature alone. The Δu and Δh of ideal gases are expressed as

$$\Delta u = u_2 - u_1 = \int_1^2 c_v(T) dT \cong c_{v,\text{avg}}(T_2 - T_1)$$
$$\Delta h = h_2 - h_1 = \int_1^2 c_p(T) dT \cong c_{p,\text{avg}}(T_2 - T_1)$$

- For ideal gases, c_v and c_p are related by

$$c_p = c_v + R$$

- The *specific* heat ratio k is defined as

$$k = \frac{c_p}{c_v}$$

Energy Analysis of Closed Systems

- For *incompressible substances* (liquids and solids), both the constant-pressure and constant-volume specific heats are identical and denoted by c :

$$c_p = c_v = c$$

- The Δu and Δh of incompressible substances are given by

$$\Delta u = \int_1^2 c(T) dT \cong c_{\text{avg}}(T_2 - T_1)$$
$$\Delta h = \Delta u + v\Delta P$$

Mass and Energy Analysis of Control Volumes

- *Conservation of mass principle*: The net mass transfer to or from a system during a process is equal to the net change (increase or decrease) in the total mass of the system during that process, and is expressed as

$$m_{\text{in}} - m_{\text{out}} = \Delta m_{\text{system}} \quad \text{and} \quad \dot{m}_{\text{in}} - \dot{m}_{\text{out}} = dm_{\text{system}}/dt$$

$$\Delta m_{\text{system}} = m_{\text{final}} - m_{\text{initial}}$$

- The relations above are also referred to as the *mass balance* and are applicable to any system undergoing any kind of process.
- The amount of mass flowing through a cross section per unit time is called the *mass flow rate*, and is expressed as

$$\dot{m} = \rho VA$$

Mass and Energy Analysis of Control Volumes

- The volume of the fluid flowing through a cross section per unit time is called the *volume flow rate* and is expressed as

$$\dot{V} = VA = \dot{m}/\rho$$

- Flow work or flow energy*: The work required to push a unit mass of fluid into or out of a control volume and is expressed as $w_{flow} = Pv$.
- In the analysis of control volumes, it is convenient to combine the flow energy and internal energy into *enthalpy*. Then the total energy of a flowing fluid is expressed as

$$\theta = h + ke + pe = h + \frac{V^2}{2} + gz$$

- The total energy transported by a flowing fluid of mass m is $E = m\theta$.
- The rate of energy transport by a fluid with a mass flow rate of $\dot{m}$ is $\dot{E} = \dot{m}\theta$.

Mass and Energy Analysis of Control Volumes

- The general energy balances for *any system* undergoing *any process* can be expressed as

$$\underbrace{E_{\text{in}} - E_{\text{out}}}_{\text{Net energy transfer by heat, work, and mass}} = \underbrace{\Delta E_{\text{system}}}_{\text{Change in internal, kinetic, potential, etc., energies}}$$

$$\underbrace{\dot{E}_{\text{in}} - \dot{E}_{\text{out}}}_{\text{Rate of net energy transfer by heat, work, and mass}} = \underbrace{dE_{\text{system}}/dt}_{\text{Rate of change in internal, kinetic, potential, etc., energies}}$$

- Thermodynamic processes involving control volumes can be considered in two groups: *steady-flow processes* and *unsteady-flow processes*.
- Taking heat transfer *to* the system and work done *by* the system to be positive quantities, the conservation of mass and energy equations for steady-flow processes are expressed as

$$\sum_{\text{in}} \dot{m} = \sum_{\text{out}} \dot{m}$$

$$\dot{Q} - \dot{W} = \sum_{\text{out}} \dot{m} \underbrace{\left(h + \frac{V^2}{2} + gz \right)}_{\text{for each exit}} - \sum_{\text{in}} \dot{m} \underbrace{\left(h + \frac{V^2}{2} + gz \right)}_{\text{for each inlet}}$$

Mass and Energy Analysis of Control Volumes

- These are the most general forms of the equations for steady-flow processes. For single-stream (one-inlet–one-exit) systems such as nozzles, diffusers, turbines, compressors, and pumps, they simplify to

$$\dot{m}_1 = \dot{m}_2 \longrightarrow \frac{1}{v_1} V_1 A_1 = \frac{1}{v_2} V_2 A_2$$
$$\dot{Q} - \dot{W} = \dot{m} \left[h_2 - h_1 + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1) \right]$$

- Most unsteady-flow processes can be modeled as a *uniform-flow process*, which requires that the fluid flow at any inlet or exit is uniform and steady, and thus the fluid properties do not change with time or position over the cross section of an inlet or exit. If they do, they are averaged and treated as constants for the entire process.

Mass and Energy Analysis of Control Volumes

- By neglecting KE and PE of the control volume, the mass and energy balance relations for a *uniform-flow system* are expressed as

$$m_{\text{in}} - m_{\text{out}} = \Delta m_{\text{system}}$$

$$Q - W = \sum_{\text{out}} mh - \sum_{\text{in}} mh + (m_2 u_2 - m_1 u_1)_{\text{system}}$$

$$Q = Q_{\text{net,in}} = Q_{\text{in}} - Q_{\text{out}}$$

$$W = W_{\text{net,out}} = W_{\text{out}} - W_{\text{in}}$$

- When solving thermodynamic problems, it is recommended that the general form of the energy balance $E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$ be used for all problems, and simplify it for the particular problem instead of using the specific relations given here for different processes.

The Second Law of Thermodynamics

- The *second law of thermodynamics* states that processes occur in a certain direction, not in any direction.
- A process does not occur unless it satisfies both the *first and the second laws of thermodynamics*.
- *Thermal energy reservoirs or heat reservoirs*: Bodies that can *absorb* or *reject* finite amounts of heat *isothermally*.
- Work can be converted to heat directly, but heat can be converted to work only by some devices called *heat engines*.
- The *thermal efficiency* of a heat engine is defined as

$$\eta_{\text{th}} = \frac{W_{\text{net,out}}}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

$W_{\text{net,out}}$ is the net work output of the heat engine
 Q_H is the amount of heat supplied to the engine
 Q_L is the amount of heat rejected by the engine

The Second Law of Thermodynamics

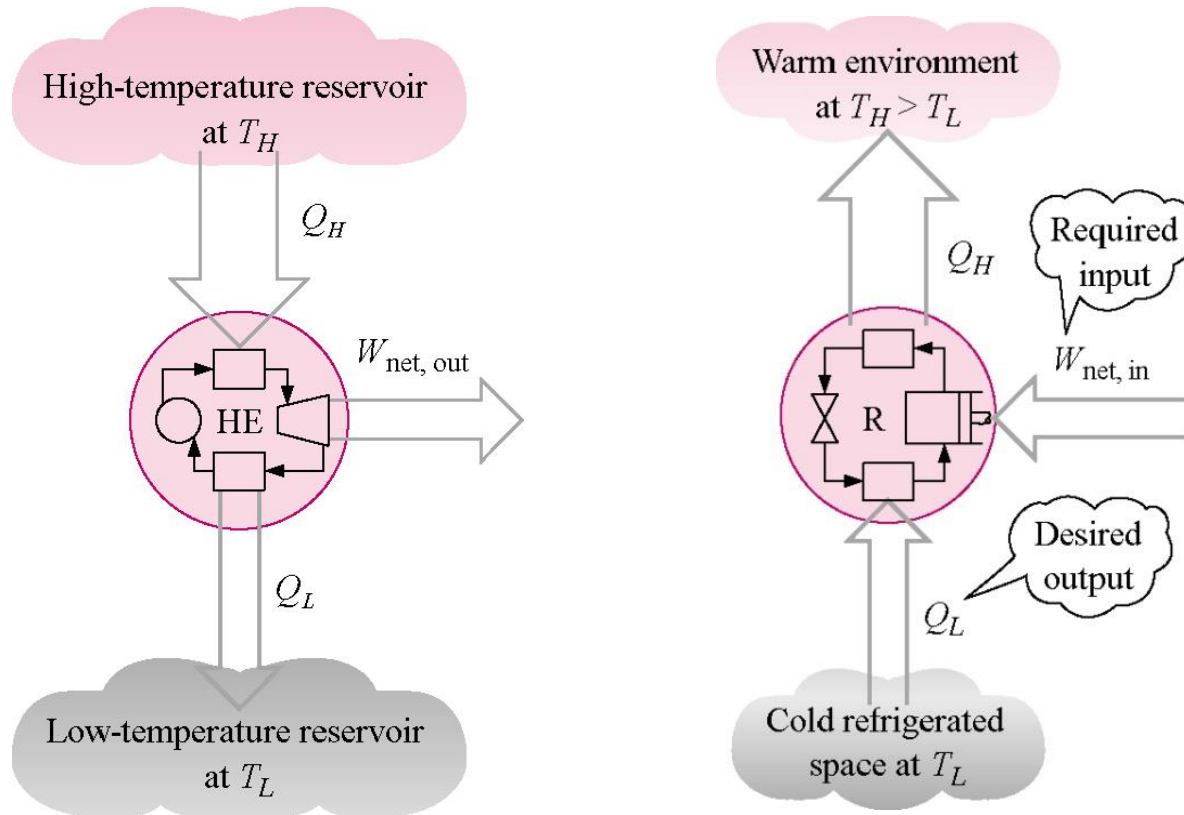
- Refrigerators and heat pumps are devices that absorb heat from low-temperature media and reject it to higher-temperature ones.
- The performance of a refrigerator or a heat pump is expressed in terms of the *coefficient of performance*, which is defined as

$$\text{COP}_R = \frac{Q_L}{W_{\text{net,in}}} = \frac{1}{Q_H/Q_L - 1}$$

$$\text{COP}_{\text{HP}} = \frac{Q_H}{W_{\text{net,in}}} = \frac{1}{1 - Q_L/Q_H}$$

- Kelvin–Planck statement:** no heat engine can produce a net amount of work while exchanging heat with a single reservoir only.
- Clausius statement:** no device can transfer heat from a cooler body to a warmer one without leaving an effect on the surroundings.
- Perpetual-motion machine:** Any device that violates the first or the second law of thermodynamics

The Second Law of Thermodynamics



$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

$$COP = \frac{\text{Desired Result}}{\text{Required Input}}$$

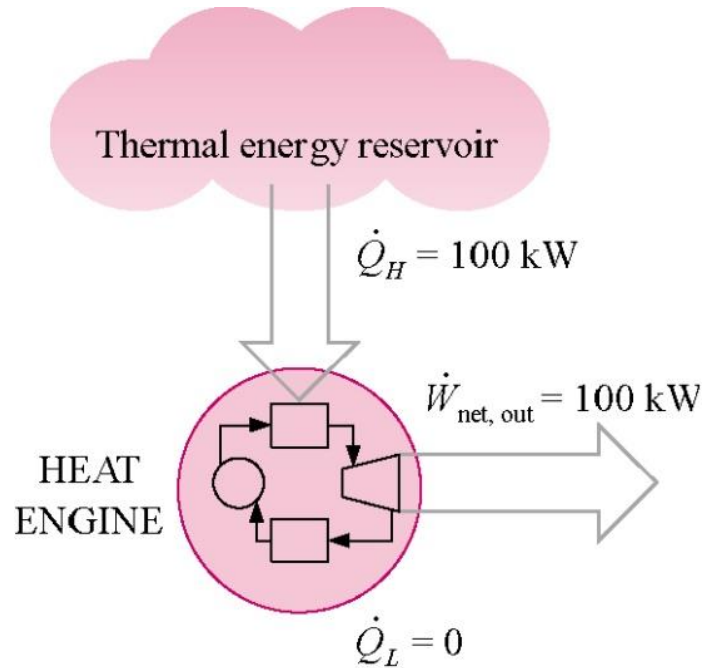
$$COP_R = \frac{Q_L}{Q_H - Q_L}$$

$$COP_{HP} = \frac{Q_H}{W_{net, in}} = \frac{Q_H}{Q_H - Q_L}$$

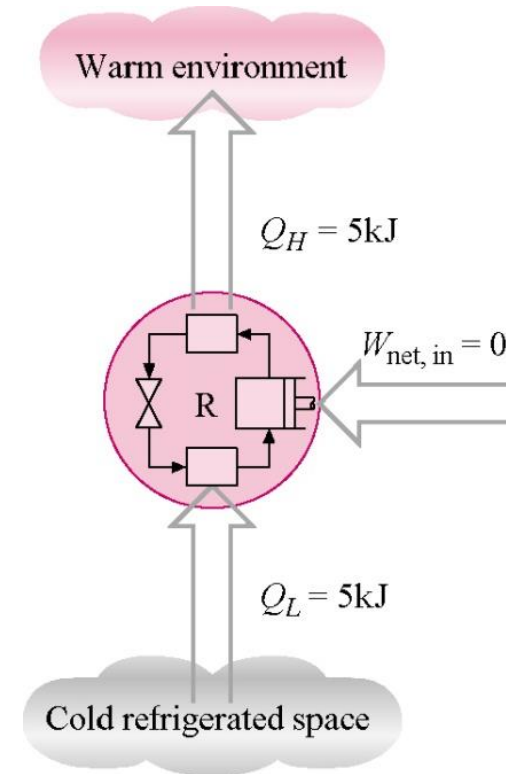
$$(Q_L - Q_H) - (0 - W_{in}) = \Delta U_{cycle} = 0$$

$$W_{in} = W_{net, in} = Q_H - Q_L$$

The Second Law of Thermodynamics



Heat engine that violates the Kelvin-Planck statement of the second law



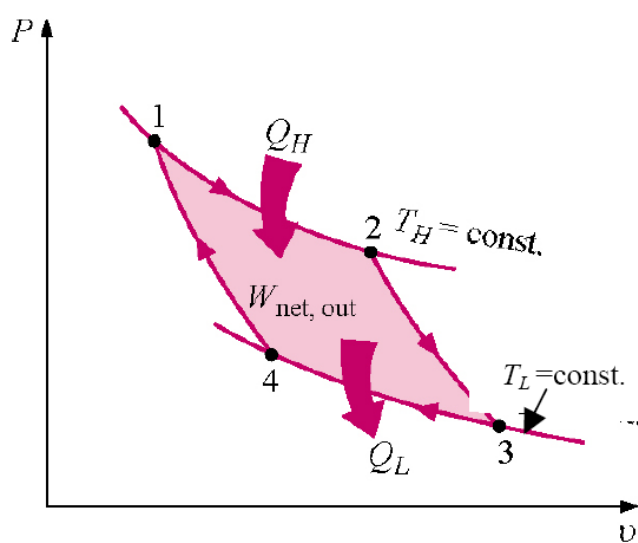
Heat pump that violates the Clausius statement of the second law

The Second Law of Thermodynamics

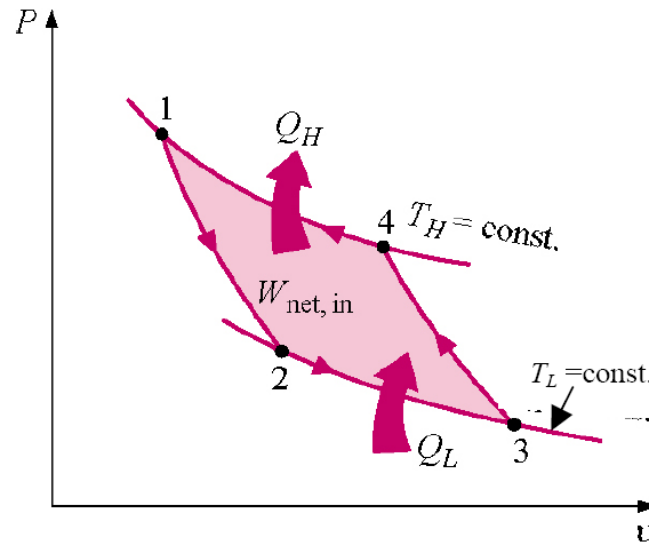
- A process is said to be *reversible* if both the *system* and the *surroundings* can be restored to their original conditions. Any other process is *irreversible*. The effects such as friction, non-quasi-equilibrium expansion or compression, and heat transfer through a finite temperature difference render a process irreversible and are called *irreversibilities*.
- *Carnot cycle*: a reversible cycle that is composed of four reversible processes, two isothermal and two adiabatic.
- *Carnot principles*: the thermal efficiencies of all reversible heat engines operating between the same two reservoirs are the same, and that no heat engine is more efficient than a reversible one operating between the same two reservoirs.
- *Thermodynamic temperature scale*,

$$\left(\frac{Q_H}{Q_L}\right)_{\text{rev}} = \frac{T_H}{T_L}$$

The Second Law of Thermodynamics



P-v diagram for Carnot heat engine



P-v diagram for Carnot refrigerator

The Carnot Cycle

Process 1-2:

Reversible isothermal heat addition at high temperature, $T_H > T_L$, to the working fluid in a piston-cylinder device that does some boundary work.

Process 2-3:

Reversible adiabatic expansion during which the system does work as the working fluid temperature decreases from T_H to T_L .

Process 3-4:

The system is brought in contact with a heat reservoir at $T_L < T_H$ and a **reversible isothermal** heat exchange takes place while work of compression is done on the system.

Process 4-1:

A **reversible adiabatic** compression process increases the working fluid temperature from T_L to T_H .

The Second Law of Thermodynamics

- A heat engine that operates on the reversible Carnot cycle is called a *Carnot heat engine*. The thermal efficiency of a Carnot heat engine, as well as all other reversible heat engines, is given by

$$\eta_{\text{th,rev}} = 1 - \frac{T_L}{T_H}$$

- The COPs of reversible refrigerators and heat pumps are given in a similar manner as

$$\text{COP}_{\text{R,rev}} = \frac{1}{T_H/T_L - 1}$$

$$\text{COP}_{\text{HP,rev}} = \frac{1}{1 - T_L/T_H}$$

- These are the highest COPs a refrigerator or a heat pump operating between the temperature limits of T_H and T_L can have. It is true for heat engines as well.

Entropy

- **Entropy**: quantitative measure of microscopic disorder for a system. It is defined as a new property by second law of thermodynamics.
- Any quantity whose cyclic integral is zero is a property, and entropy is defined as

$$dS = \left(\frac{dQ}{T} \right)_{\text{int rev}}$$

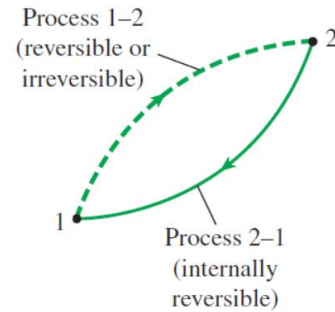
- For the special case of an internally reversible, isothermal process, it gives

$$\Delta S = \frac{Q}{T_0}$$

- **Increase of entropy principle,**

$$\oint \frac{\delta Q}{T} \leq 0 \Rightarrow \int_1^2 \frac{\delta Q}{T} + \int_2^1 \left(\frac{\delta Q}{T} \right)_{\text{int rev}} \leq 0 \Rightarrow S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T} \Rightarrow dS \geq \frac{\delta Q}{T}$$

$$\Delta S_{\text{sys}} = S_2 - S_1 = \int_1^2 \frac{\delta Q_{\text{net}}}{T} + S_{\text{gen}} \quad \left(\frac{kJ}{K} \right)$$



Entropy

- S_{gen} is the *entropy generated* during the process. $S_{\text{gen}} \geq 0$
- Entropy change is caused by heat transfer, mass flow, and irreversibilities.
- Heat transfer to a system increases the entropy, and heat transfer from a system decreases it.
- The effect of irreversibilities is always to increase the entropy.

The *entropy-change* and *isentropic relations* for a process can be summarized as follows:

1- Pure substances:

Any process:

$$\Delta s = s_2 - s_1$$

Isentropic process:

$$s_2 = s_1$$

Entropy

2- Incompressible substances:

Any process:

$$s_2 - s_1 = c_{\text{avg}} \ln \frac{T_2}{T_1}$$

Isentropic process:

$$T_2 = T_1$$

3- Ideal gases:

a- Constant specific heats (approximate treatment):

Any process:

$$s_2 - s_1 = c_{v,\text{avg}} \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

$$s_2 - s_1 = c_{p,\text{avg}} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

Entropy

Isentropic process:

$$\left(\frac{T_2}{T_1}\right)_{s=\text{const.}} = \left(\frac{v_1}{v_2}\right)^{k-1}$$

$$\left(\frac{T_2}{T_1}\right)_{s=\text{const.}} = \left(\frac{P_2}{P_1}\right)^{(k-1)/k}$$

$$\left(\frac{P_2}{P_1}\right)_{s=\text{const.}} = \left(\frac{v_1}{v_2}\right)^k$$

b- Variable specific heats (exact treatment):

Any process:

$$s_2 - s_1 = s_2^\circ - s_1^\circ - R \ln \frac{P_2}{P_1}$$

Isentropic process:

$$s_2^\circ = s_1^\circ + R \ln \frac{P_2}{P_1}$$

$$\left(\frac{P_2}{P_1}\right)_{s=\text{const.}} = \frac{P_{r2}}{P_{r1}}$$

$$\left(\frac{v_2}{v_1}\right)_{s=\text{const.}} = \frac{v_{r2}}{v_{r1}}$$

where P_r is the *relative pressure* and v_r is the *relative specific volume*. The function s° depends on temperature only.

Entropy

- The *steady-flow work* for a reversible process can be expressed in terms of the fluid properties as

$$w_{\text{rev}} = - \int_1^2 v \, dP - \Delta \text{ke} - \Delta \text{pe}$$

For incompressible substances

$$\Rightarrow w_{\text{rev}} = -v(P_2 - P_1) - \Delta \text{ke} - \Delta \text{pe}$$

- v should be kept as small as possible during a compression process to minimize the work input and as large as possible during an expansion process to maximize the work output.

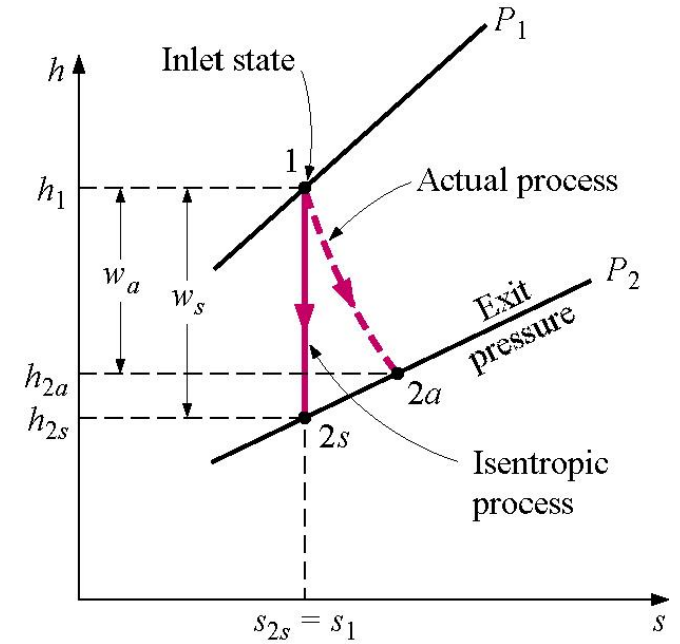
The reversible work inputs to a compressor compressing an ideal gas from T_1, P_1 to P_2

$$\begin{aligned} \text{Isentropic:} \quad (Pv^k = \text{constant}) \quad w_{\text{comp,in}} &= \frac{kR(T_2 - T_1)}{k - 1} = \frac{kRT_1}{k - 1} \left[\left(\frac{P_2}{P_1} \right)^{(k-1)/k} - 1 \right] \\ \text{Polytropic:} \quad (Pv^n = \text{constant}) \quad w_{\text{comp,in}} &= \frac{nR(T_2 - T_1)}{n - 1} = \frac{nRT_1}{n - 1} \left[\left(\frac{P_2}{P_1} \right)^{(n-1)/n} - 1 \right] \\ \text{Isothermal:} \quad (Pv = \text{constant}) \quad w_{\text{comp,in}} &= RT \ln \frac{P_2}{P_1} \end{aligned}$$

Entropy

- Most steady-flow devices operate under adiabatic conditions, and the ideal process for these devices is the isentropic process.
- The parameter that describes how efficiently a device approximates a corresponding isentropic device is called *isentropic* or *adiabatic efficiency*.

$$\eta_T = \frac{\text{Actual turbine work}}{\text{Isentropic turbine work}} = \frac{w_a}{w_s} \cong \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$$
$$\eta_C = \frac{\text{Isentropic compressor work}}{\text{Actual compressor work}} = \frac{w_s}{w_a} \cong \frac{h_{2s} - h_1}{h_{2a} - h_1}$$
$$\eta_N = \frac{\text{Actual KE at nozzle exit}}{\text{Isentropic KE at nozzle exit}} = \frac{V_{2a}^2}{V_{2s}^2} \cong \frac{h_1 - h_{2a}}{h_1 - h_{2s}}$$



Entropy

- The entropy balance for any system undergoing any process can be expressed in the general form as

$$\underbrace{S_{\text{in}} - S_{\text{out}}}_{\text{Net entropy transfer by heat and mass}} + \underbrace{S_{\text{gen}}}_{\text{Entropy generation}} = \underbrace{\Delta S_{\text{system}}}_{\text{Change in entropy}}$$
$$\underbrace{\dot{S}_{\text{in}} - \dot{S}_{\text{out}}}_{\text{Rate of net entropy transfer by heat and mass}} + \underbrace{\dot{S}_{\text{gen}}}_{\text{Rate of Entropy generation}} = \underbrace{dS_{\text{system}}/dt}_{\text{Rate of change in entropy}}$$

- For a general *steady-flow process* it simplifies to

$$\dot{S}_{\text{gen}} = \sum \dot{m}_e s_e - \sum \dot{m}_i s_i - \sum \frac{\dot{Q}_k}{T_k}$$