Temperature of a lake (or any water body) is lower than atmospheric temperature. Why ?

Air
25°C
$\phi = 10\%$
P_v

$P_v = P_{sat\ @\ T}$

T

Lake

Water

Salt

Salty water
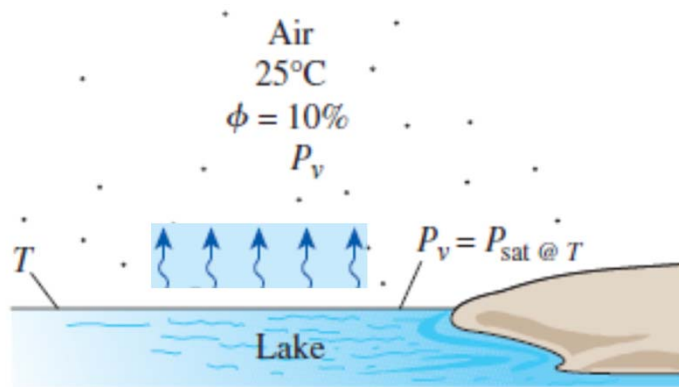
Close to the surface of the lake air
Water vapor pressure is equal to saturation
Pressure at the temperature of the lake.

However away from the surface, water vapor
Pressure is lower

Any concentration difference between two
regions leads to diffusion (e.g. dissolution of
Salt in water).
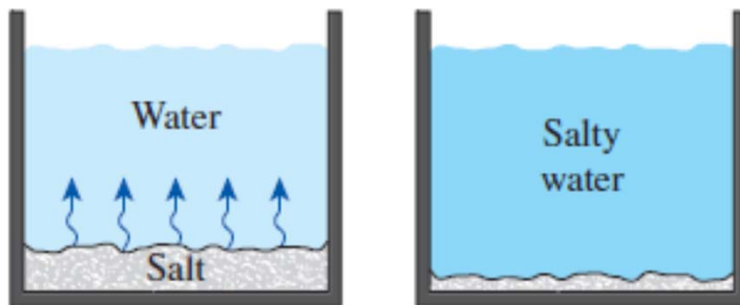
Water vapor from the surface diffuses to
Atmosphere. This leads to depletion of
Water vapor near the surface and further
Evaporation. And the process continues !!

The energy required from the evaporation
Is taken from the lake itself. This
Leads to cooling of lakes (or water bodies)

Difference between boiling and evaporation

Air
25°C
$\phi = 10\%$
P_v

$P_v = P_{sat \, @ \, T}$

T
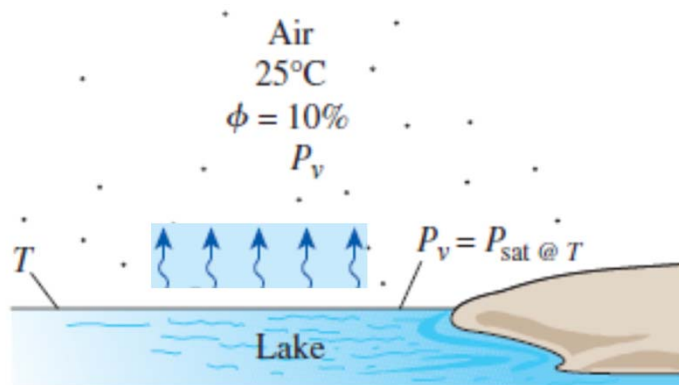
Lake

Evaporation occurs at the Liquid-gas interface. evaporation occurs from the surface of lakes, from the surface of (porous) earthen pots, during drying of clothes, fruits, vegetables in the atmosphere. Another examples is evaporation of sweat from the skin surface.

Boiling occurs at the liquid solid interface.
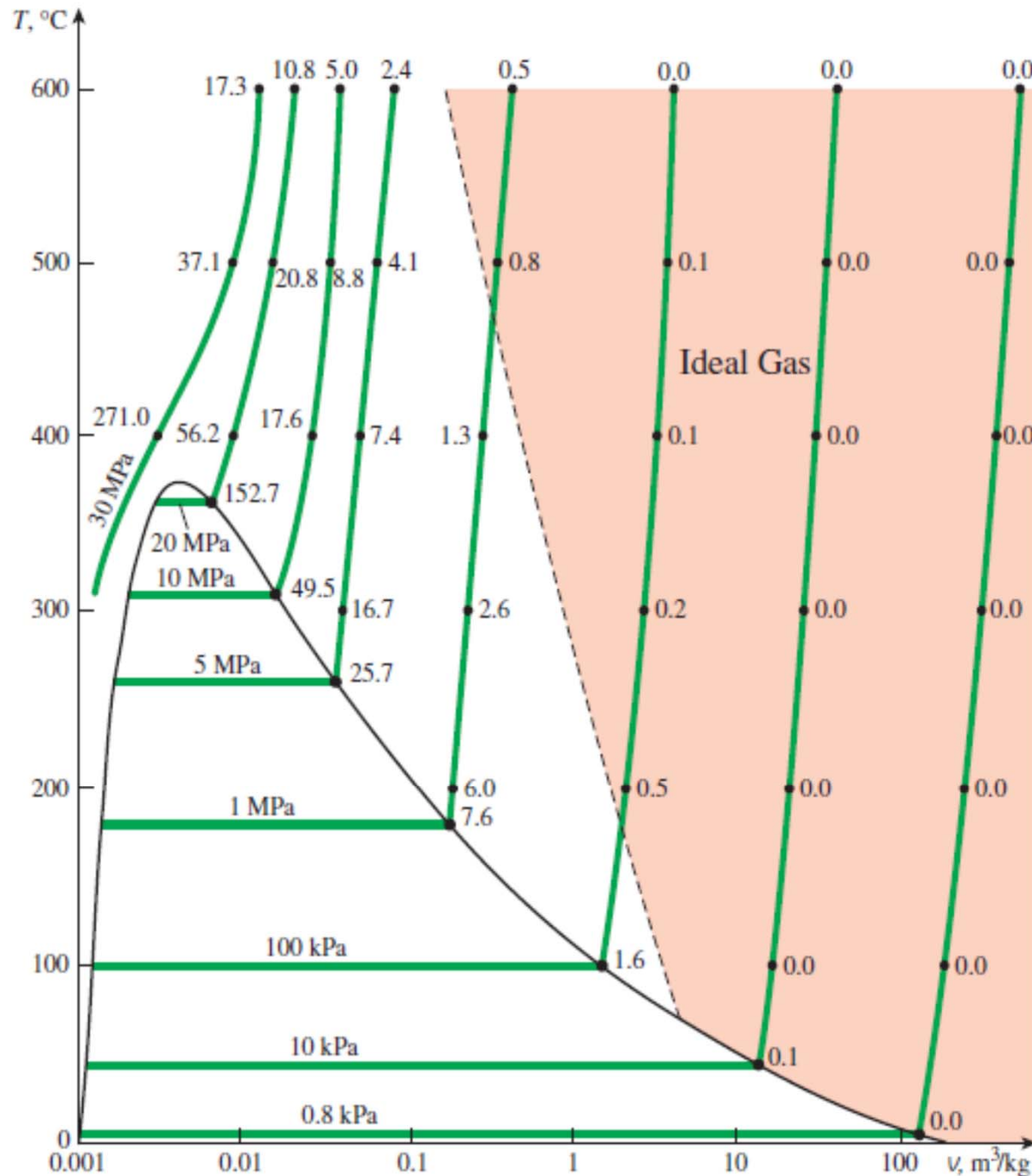
In boiling of water in an open pan, bubbles containing steam (pure water vapor without air) are generated at the bottom or side surface of the pan.

These steam bubble have the same pressure as water.

These bubbles, after reaching a certain size, rise to the top and the steam then escapes into the atmosphere.

Can water vapor be considered as ideal gas ?

$$Error(\%) = \left|\frac{v_{act}-v_{ideal}}{v_{act}}\right| \times 100$$

In the colored region, ideal gas equation of state yields error < 1%.

Below 100 kPa, ideal gas equation of state is fairly accurate for superheated Water vapor.

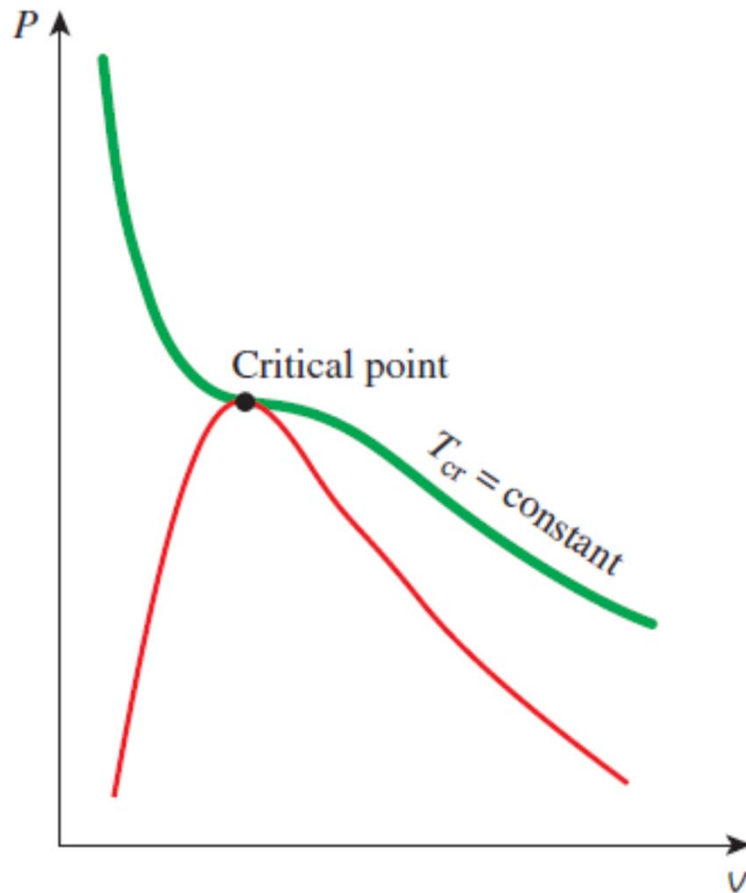At high pressures, near the Saturated vapor curve, and close the the critical point, error increases.

Other equations of state :

To describe non-ideal behaviour, other EOS have been proposed. These are semi-empirical equations. The parameters in the equations are obtained by fitting to Experimental data.

van der Waals

Berthelet

Redlich-Kwang

Beattie-Bridgeman

Benedict-Webb-Rubin

Strobridge

Virial

Van der Waals equations of state :

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT$$

Consists of two constants a and b

The term $\frac{a}{v^2}$ accounts for intermolecular forces

The constant 'b' takes into account the volume occupied by the molecules

The constants a and b are determined based on the condition that critical point is an inflection point on the critical isotherm

$$\left(\frac{\partial P}{\partial v}\right)_{T=T_{cr}} = 0 \qquad \left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_{cr}} = 0$$

Van der Waals equations of state :

Upon solving the equations on the previous slides, we get

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

Thus the values of a and b can be calculated from critical properties Listed in Table A-1. Note that in the above equations, 'v' is the specific volume on per unit Mass basis (SI unit : m^3/kg), $R = R_u/M$ where M is the molecular weight.

Substance	Formula	Molar mass, M kg/kmol	Gas constant, R kJ/kg·K*	Critical-point properties	
				Temperature, K	Pressure, MPa
Nitrogen	N_2	28.013	0.2968	126.2	3.39

For N_2, $a = 0.175 \text{ m}^6\text{·kPa/kg}^2$

$b = 0.00138 \text{ m}^3/\text{kg}$

$R = Ru/M = 8.314/28.013 = 0.2968$

For T = 175 K, v = 0.00375 m^3/kg

From the van der Waals ESO, we get

P = 9471 kPa

Actual value of **P$_{act}$ = 10000 kPa**, thus an error of **5.3 %**

Beattie-Bridgemann equation of state :

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

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

No. of constants = 5, Accurate upto densities less than or equal to 0.8 times the critical density

(a) When P is in kPa, $\bar{v}$ is in m³/kmol, T is in K, and R_u = 8.314 kPa·m³/kmol·K, the five constants in the Beattie-Bridgeman equation are as follows:

Gas	A_0	a	B_0	b	c
Air	131.8441	0.01931	0.04611	−0.001101	4.34×10^4
Argon, Ar	130.7802	0.02328	0.03931	0.0	5.99×10^4
Carbon dioxide, CO_2	507.2836	0.07132	0.10476	0.07235	6.60×10^5
Helium, He	2.1886	0.05984	0.01400	0.0	40
Hydrogen, H_2	20.0117	−0.00506	0.02096	−0.04359	504
Nitrogen, N_2	136.2315	0.02617	0.05046	−0.00691	4.20×10^4
Oxygen, O_2	151.0857	0.02562	0.04624	0.004208	4.80×10^4

For N_2,

$A = 102.29$

$B = 0.05378$

$c = 4.2 \times 10^4$

For T = 175 K,   v = 0.00375 m³/kg

$\bar{v} = Mv = (28.013)(0.00375)$

$\bar{v} = 0.10505$ m³/kmol

From the above equation, we get
P = 10,110 kPa

Actual value of **P_{act} = 10000 kPa**, thus an error of **1.1 %**

Benedict-Webb-Rubin equation of state :

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

No. of constants = 8, Accurate upto densities less than or equal to 2.5 times the critical density

(b) When P is in kPa, $\bar{v}$ is in m^3/kmol, T is in K, and R_u = 8.314 kPa·m^3/kmol·K, the eight constants in the Benedict-Webb-Rubin equation are as follows:

Gas	a	A_0	b	B_0	c	C_0	α	γ
n-Butane, C_4H_{10}	190.68	1021.6	0.039998	0.12436	3.205×10^7	1.006×10^8	1.101×10^{-3}	0.0340
Carbon dioxide, CO_2	13.86	277.30	0.007210	0.04991	1.511×10^6	1.404×10^7	8.470×10^{-5}	0.00539
Carbon monoxide, CO	3.71	135.87	0.002632	0.05454	1.054×10^5	8.673×10^5	1.350×10^{-4}	0.0060
Methane, CH_4	5.00	187.91	0.003380	0.04260	2.578×10^5	2.286×10^6	1.244×10^{-4}	0.0060
Nitrogen, N_2	2.54	106.73	0.002328	0.04074	7.379×10^4	8.164×10^5	1.272×10^{-4}	0.0053

For N_2,

$a = 2.54$ $A_0 = 106.73$

$b = 0.002328$ $B_0 = 0.04074$

$c = 7.379 \times 10^4$ $C_0 = 8.164 \times 10^5$

$\alpha = 1.272 \times 10^{-4}$ $\gamma = 0.0053$

For T = 175 K, v = 0.00375 m^3/kg

$\bar{v} = Mv = (28.013)(0.00375)$

$\bar{v} = 0.10505$ m^3/kmol

From the above equation, we get

P = 10,009 kPa

Actual value of **P_{act} = 10000 kPa**, thus an error of **0.09 %**

Comparison of P calculated for N_2 from different EOS :

For T = 175 K,   v = 0.00375 m^3/kg P_{act} = 10000 kPa

EOS	P (CALCULATED) kPa	ERROR %
Ideal gas	13851	38.5
van der Waals	9471	5.3
Beattie-Bridgemann	10110	1.1
Benedict-Webb-Rubin	10009	0.09

More on ideal gas :

According to state postulate, any intensive property including specific internal energy (u) can be considered as a function of (T,v) for a gas phase.

Joule performed an interesting experiment (see picture below) There are two rigid spherical containers connected through a valve and immersed in water. One of the containers contains air at a certain pressure and the other container is evacuated. Water is in thermal equilibrium with air.

The valve is now opened and air expands into the other container. It is observed that there is no change in the temperature of water measured by the thermometer after the process is complete.
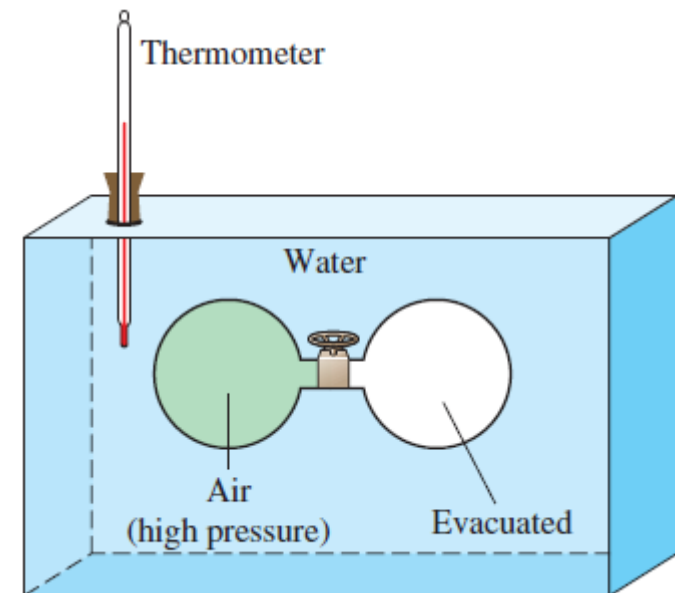
More on ideal gas :

Analysis of Joule's experiment:

Since containers are rigid, no work is done by air on the surroundings. Hence first law of thermodynamics takes the form: $\Delta U = Q_{in}$ [our system is the gas inside the container(s)]

Since water temperature does not change, there is no heat gained or lost by water. This means that $Q_{in} = 0$

This implies that $\Delta U = 0$

Thus, for a given mass of air, U is independent of volume.

However this is only true for gases which (at least) approximately behave as ideal gas !
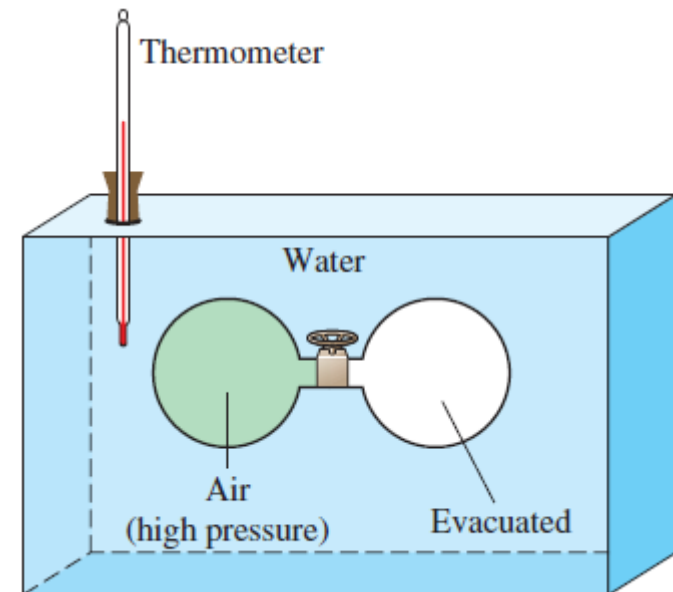
Thermometer

Water

Air
(high pressure)

Evacuated

More on ideal gas :

According to state postulate, any intensive property including specific internal energy (u) can be considered as a function of (T,v) for a gas phase.

Experimentally (for an ideal gas) it has been shown that for an ideal gas, internal energy U is independent of V. This implies that   u = u (T), i.e., u is independent of v

Since h = u + Pv = u + RT,   h = h(T) for an ideal gas

Note : if the same experiment (see previous slides) is performed for a <u>non-ideal gas</u>, there will be a heat exchange between gas and water which will result in a change of temperature. In Joule's experiment the temperature and pressure conditions were such that gas was closely approximating the ideal gas behavior.

Specific heats :

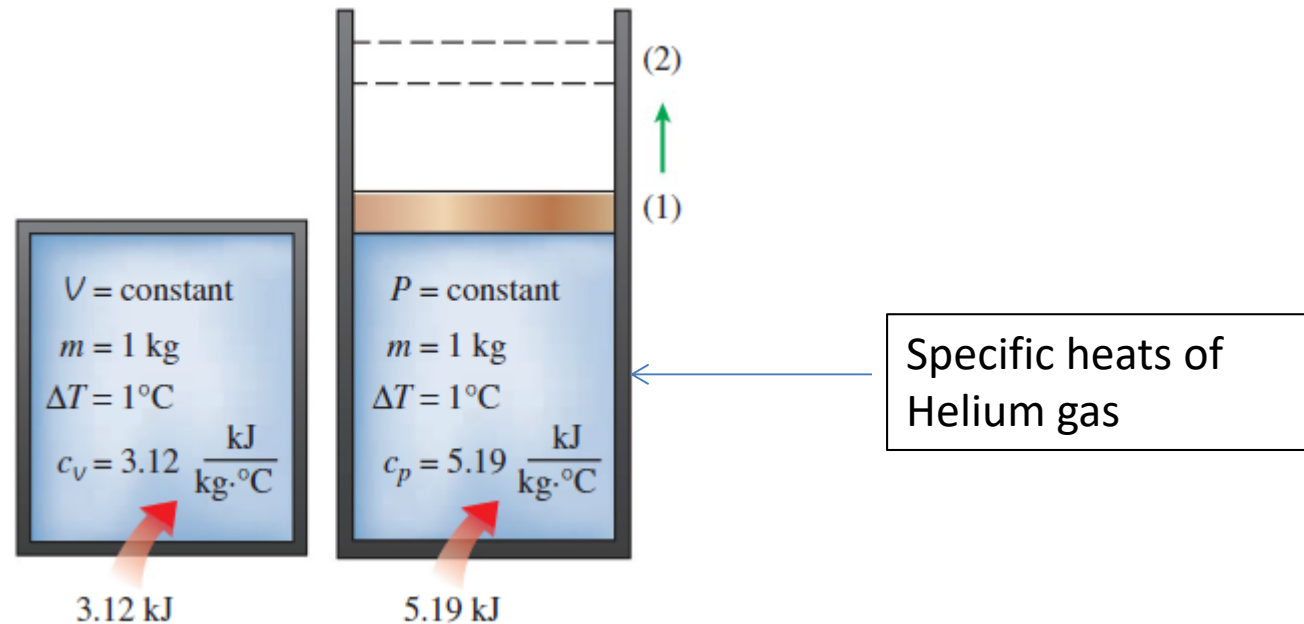Mathematically,

$$C_v = \frac{1}{m}\left(\frac{\partial Q_{in}}{\partial T}\right)_V$$

$$C_P = \frac{1}{m}\left(\frac{\partial Q_{in}}{\partial T}\right)_P$$

m = total mass
of substance

$V = $ constant
$m = 1$ kg
$\Delta T = 1°C$
$c_v = 3.12 \ \dfrac{kJ}{kg·°C}$

3.12 kJ

$P = $ constant
$m = 1$ kg
$\Delta T = 1°C$
$c_p = 5.19 \ \dfrac{kJ}{kg·°C}$

5.19 kJ

(2)

(1)

Specific heats of
Helium gas

For a process at constant volume, work output is zero. Hence,

$$dU = dQ_{in}$$

This leads to the following important relation :

$$C_v = \frac{1}{m}\left(\frac{\partial U}{\partial T}\right)_v = \left(\frac{\partial u}{\partial T}\right)_v$$

u = specific internal energy

Fro a constant P process, it was shown   : $dH = dQ_{in}$

This implies that

$$C_P = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial h}{\partial T}\right)_P$$

h = specific enthalpy

Note: A constant P process implies that mechanical equilibrium is maintained. Because we can only control P_{ext} and we have no direct control over P. Hence constant P can ONLY be maintained by ensuring that P_{ext} is constant and mechanical equilibrium is maintained during the process

Specific heats of ideal gases :

Since u is a function only of T and is independent of v

$$C_v = \frac{1}{m}\left(\frac{dU}{dT}\right) = \frac{du}{dT}$$

For an ideal gas, there is NO requirement of constant V in the derivatives for C_P

Also, h is a function only of T and is independent of P for an ideal gas. Hence,

$$C_P = \frac{1}{m}\left(\frac{dH}{dT}\right) = \frac{dh}{dT}$$

For an ideal gas, there is NO requirement of constant P in the derivatives for C_P

Note that C_V and C_P are both functions only of T for an ideal gas. Many real gases approach ideal gas behavior at low pressures. Hence the low pressure specific heats of gases are known as ideal gas specific heats or zero pressure specific heats and are denoted by adding a subscript '0' : C_{V0} and C_{P0}.

Relations between specific heats of ideal gases :

As seen in a previous lecture, enthalpy is defined as

$$H = U + PV$$

Thus, on a basis of unit mass of substance we have

$$h = u + Pv$$

For an ideal gas, the equation of state is $Pv = RT$.
Substituting this in above equation, we get

$$h = u + RT$$

Taking derivative of both sides with respect to T, we get

$$\boxed{C_P = C_V + R}$$

On a molar basis : $\boxed{\overline{C}_P = \overline{C}_V + R_u}$

Here $\overline{C}_P$ and $\overline{C}_V$ are molar specific heats and R_u is universal gas constant

Another important quantity related to specific heats is the ratio of specific heats, defined as $k = C_P / C_V$

Zero pressure (ideal gas) specific heats C_{V0} and C_{P0} :
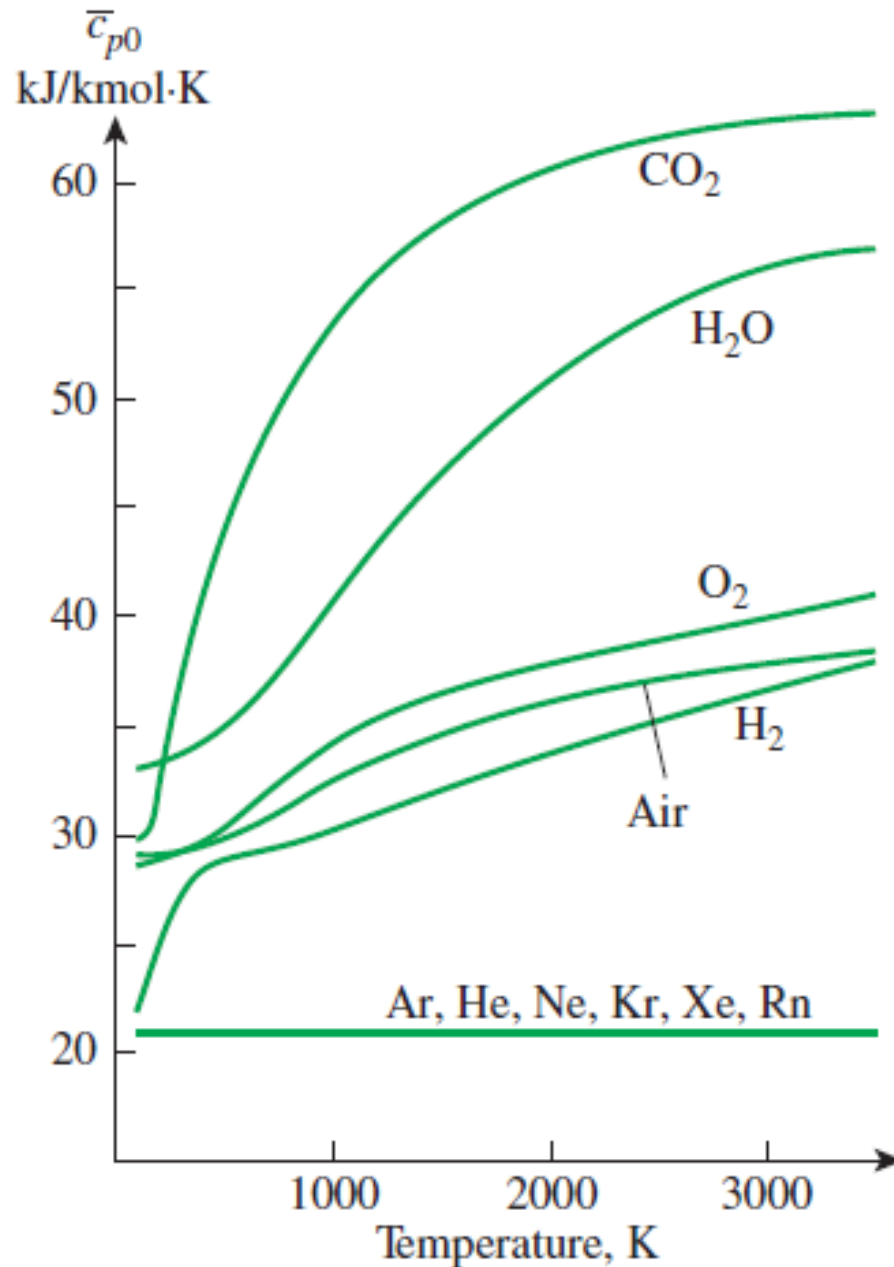
The "bar" on the $\overline{C_{P0}}$ indicates that specific heat is on per mole basis

Since Ar, He, Ne, Kr, Xe, Rn are monatomic gases, the ideal gas or zero pressure specific heats of these gases remain constant.

For polyatomic gases, the specific heats increase with temperature due to translational, rotational and vibrational components of kinetic energy

Zero pressure (ideal gas) specific heats C_{V0} and C_{P0} :

Values for various gases are listed in Tables A-2(a), A-2(b), A-2(c)
Table A-2(a) give specific heat values at 300 K (reproduced below)

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	k
Air	—	0.2870	1.005	0.718	1.400
Argon	Ar	0.2081	0.5203	0.3122	1.667
Butane	C_4H_{10}	0.1433	1.7164	1.5734	1.091
Carbon dioxide	CO_2	0.1889	0.846	0.657	1.289
Carbon monoxide	CO	0.2968	1.040	0.744	1.400
Ethane	C_2H_6	0.2765	1.7662	1.4897	1.186
Ethylene	C_2H_4	0.2964	1.5482	1.2518	1.237
Helium	He	2.0769	5.1926	3.1156	1.667
Hydrogen	H_2	4.1240	14.307	10.183	1.405
Methane	CH_4	0.5182	2.2537	1.7354	1.299
Neon	Ne	0.4119	1.0299	0.6179	1.667
Nitrogen	N_2	0.2968	1.039	0.743	1.400
Octane	C_8H_{18}	0.0729	1.7113	1.6385	1.044
Oxygen	O_2	0.2598	0.918	0.658	1.395
Propane	C_3H_8	0.1885	1.6794	1.4909	1.126
Steam	H_2O	0.4615	1.8723	1.4108	1.327

Note that the subscript '0' is not always used. Sometimes Cv0 (zero pressure Specific heat) is denoted as Cv. Similarly Cp0 is denoted as Cp

Zero pressure (ideal gas) specific heats C_{V0} and C_{P0} :

Table A-2(b) give specific heat values at various temperatures

Partially reproduced below

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	c_p kJ/kg·K	c_v kJ/kg·K	k
	Air			Carbon dioxide, CO_2			Carbon monoxide, CO		
250	1.003	0.716	1.401	0.791	0.602	1.314	1.039	0.743	1.400
300	1.005	0.718	1.400	0.846	0.657	1.288	1.040	0.744	1.399
350	1.008	0.721	1.398	0.895	0.706	1.268	1.043	0.746	1.398
400	1.013	0.726	1.395	0.939	0.750	1.252	1.047	0.751	1.395
450	1.020	0.733	1.391	0.978	0.790	1.239	1.054	0.757	1.392
500	1.029	0.742	1.387	1.014	0.825	1.229	1.063	0.767	1.387
550	1.040	0.753	1.381	1.046	0.857	1.220	1.075	0.778	1.382
600	1.051	0.764	1.376	1.075	0.886	1.213	1.087	0.790	1.376
650	1.063	0.776	1.370	1.102	0.913	1.207	1.100	0.803	1.370
700	1.075	0.788	1.364	1.126	0.937	1.202	1.113	0.816	1.364
750	1.087	0.800	1.359	1.148	0.959	1.197	1.126	0.829	1.358
800	1.099	0.812	1.354	1.169	0.980	1.193	1.139	0.842	1.353
900	1.121	0.834	1.344	1.204	1.015	1.186	1.163	0.866	1.343
1000	1.142	0.855	1.336	1.234	1.045	1.181	1.185	0.888	1.335

Zero pressure (ideal gas) specific heats C_{V0} and C_{P0} :

Table A-2(c) give specific heat values as a function of temperature

Partially reproduced below

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	Temperature range, K	% error Max.	% error Avg.
Nitrogen	N_2	28.90	-0.1571×10^{-2}	0.8081×10^{-5}	-2.873×10^{-9}	273–1800	0.59	0.34
Oxygen	O_2	25.48	1.520×10^{-2}	-0.7155×10^{-5}	1.312×10^{-9}	273–1800	1.19	0.28
Air	—	28.11	0.1967×10^{-2}	0.4802×10^{-5}	-1.966×10^{-9}	273–1800	0.72	0.33
Hydrogen	H_2	29.11	-0.1916×10^{-2}	0.4003×10^{-5}	-0.8704×10^{-9}	273–1800	1.01	0.26
Carbon monoxide	CO	28.16	0.1675×10^{-2}	0.5372×10^{-5}	-2.222×10^{-9}	273–1800	0.89	0.37
Carbon dioxide	CO_2	22.26	5.981×10^{-2}	-3.501×10^{-5}	7.469×10^{-9}	273–1800	0.67	0.22

Zero pressure (ideal gas) specific heats C_{V0} and C_{P0} :

How to calculate Δu and Δh using tabulated specific heat data in Table A-2?

Method 1 :
$$\Delta u = \int_1^2 C_v \, dT$$

Use numerical integration by using values at discrete temperature listed in Table A-2 (b) or similar tables from other sources
(or)
Obtain Cv as a function of temperature as a polynomial function using datain Table A-2(c) or similar tables from other resources.   Then substitute in above integral and perform the integration
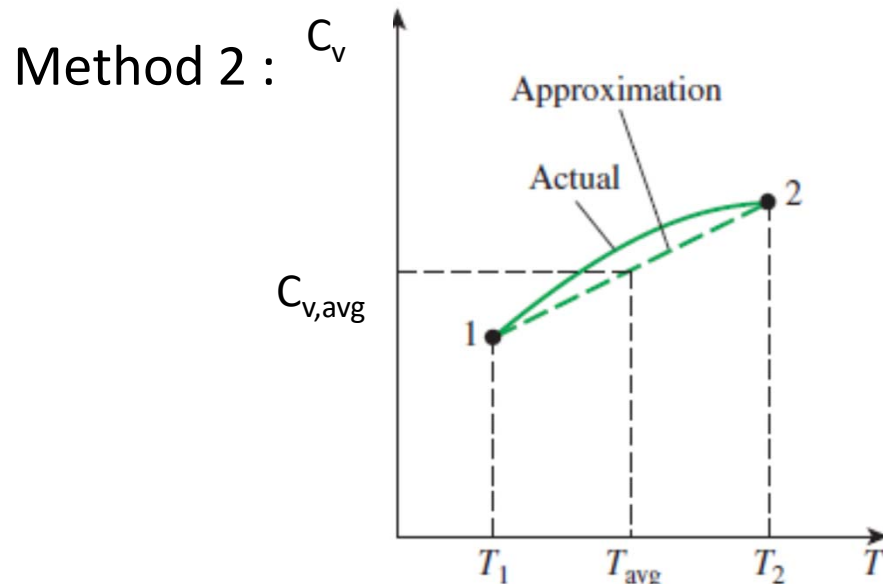
Method 2 :

$$\Delta u = \int_1^2 C_v \, dT$$

$$\approx C_{v,avg}(T_2 - T_1)$$

<u>Note</u> : Similar methods can be adopted for Δh using tabulated C_p data in Table A-2

Air at 300 K and 200 kPa is heated at constant pressure to 600 K. Determine the change in internal energy of air per unit mass, using (a) data from the air table (Table A–17), (b) the functional form of the specific heat (Table A–2c), and (c) the average specific heat value (Table A–2b).

(a) Using the tabulated values in A-17.

TABLE A–17

Ideal-gas properties of air

T	h		u		s^o
K	kJ/kg	P_r	kJ/kg	v_r	kJ/kg·K
200	199.97	0.3363	142.56	1707.0	1.29559
300	300.19	1.3860	214.07	621.2	1.70203
600	607.02	16.28	434.78	105.8	2.40902

$$\Delta u = u_2 - u_1 = (434.78 - 214.07) = 220.71 \text{ kJ/kg}$$

This is the accurate result

Air at 300 K and 200 kPa is heated at constant pressure to 600 K. Determine the change in internal energy of air per unit mass, using (a) data from the air table (Table A–17), (b) the functional form of the specific heat (Table A–2c), and (c) the average specific heat value (Table A–2b).

(b) Using the functional form in Table A-2(c)

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

$$\bar{c}_v(T) = \bar{c}_p - R_u = (a - R_u) + bT + cT^2 + dT^3$$

From Table A-2(c) data for air is reproduced below :

Substance	Formula	a	b	c	d
Air	—	28.11	0.1967×10^{-2}	0.4802×10^{-5}	-1.966×10^{-9}

$$\Delta \bar{u} = \int_1^2 \bar{c}_v \, dT = 6447 \text{ kJ/kmol (after performing integration)}$$

$$\Delta u = \frac{\Delta \bar{u}}{M} = \frac{6447 \text{ kJ/kmol}}{28.97 \text{ kg/kmol}} = 222.5 \text{ kJ/kg}$$

Comparing with the accurate value obtained in (a), <u>error is 0.8 %</u>

Air at 300 K and 200 kPa is heated at constant pressure to 600 K. Determine the change in internal energy of air per unit mass, using (a) data from the air table (Table A–17), (b) the functional form of the specific heat (Table A–2c), and (c) the average specific heat value (Table A–2b).

(c) Using the value at the average temperature

$$T_{avg} = \frac{T_1 + T_2}{2} = 450 \text{ K}$$

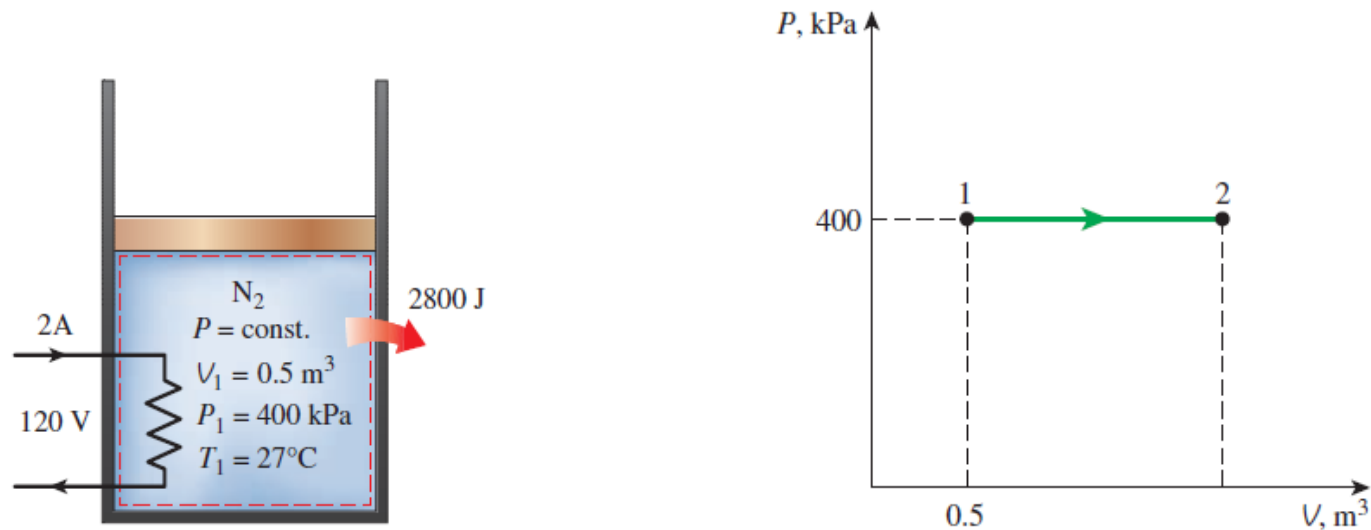$C_{v,avg}$ @ T_{avg} = 0.733 kJ/(kg.K)   From Table A-2(b)

$$\Delta u = \int_1^2 C_v \, dT$$

$$\approx C_{v,avg}(T_2 - T_1) = 220 \text{ kJ/kg}$$

Comparing with the accurate value obtained in (a), underline error is 0.4 %

Example :

A piston–cylinder device initially contains 0.5 m³ of nitrogen gas at 400 kPa and 27°C. An electric heater within the device is turned on and is allowed to pass a current of 2 A for 5 min from a 120-V source. Nitrogen expands at constant pressure, and a heat loss of 2800 J occurs during the process. Determine the final temperature of nitrogen.

$$P, kPa$$

$$400$$

$$N_2$$
$$P = const.$$
$$V_1 = 0.5 \text{ m}^3$$
$$P_1 = 400 \text{ kPa}$$
$$T_1 = 27°C$$

2A

120 V

2800 J

0.5

$$V, m^3$$

SOLUTION Nitrogen gas in a piston–cylinder device is heated by an electric resistance heater. Nitrogen expands at constant pressure while some heat is lost. The final temperature of nitrogen is to be determined.

Assumptions **1** Nitrogen is an ideal gas since it is at a high temperature and low pressure relative to its critical-point values of −147°C, and 3.39 MPa. **2** The system is stationary and thus the kinetic and potential energy changes are zero, $\Delta KE = \Delta PE = 0$ and $\Delta E = \Delta U$. **3** The pressure remains constant during the process and thus $P_2 = P_1$. **4** Nitrogen has constant specific heats at room temperature.

Analysis We take the contents of the cylinder as the *system* This is a *closed system* since no mass crosses the system boundary during the process. We observe that a piston–cylinder device typically involves a moving boundary and thus boundary work, W_b. Also, heat is lost from the system and electrical work W_e is done on the system.

First, let us determine the electrical work done on the nitrogen:

$$W_e = VI\,\Delta t = (120\ \text{V})(2\ \text{A})(5\times 60\ \text{s})\left(\frac{1\ \text{kJ/s}}{1000\ \text{VA}}\right) = 72\ \text{kJ}$$

The mass of nitrogen is determined from the ideal-gas relation:

$$m = \frac{P_1 V_1}{RT_1} = \frac{(400\ \text{kPa})(0.5\ \text{m}^3)}{(0.297\ \text{kPa·m}^3/\text{kg·K})(300\ \text{K})} = 2.245\ \text{kg}$$

$$W_{e,in} - Q_{out} - W_{b,out} = \Delta U$$

$$W_{e,in} - Q_{out} = \Delta H = m(h_2 - h_1) = mc_p(T_2 - T_1)$$

since $\Delta U + W_b = \Delta H$ for a closed system undergoing a quasi-equilibrium expansion or compression process at constant pressure. From Table A–2a, $c_p = 1.039$ kJ/kg·K for nitrogen at room temperature. The only unknown quantity in the previous equation is T_2, and it is found to be

$$72\ \text{kJ} - 2.8\ \text{kJ} = (2.245\ \text{kg})(1.039\ \text{kJ/kg·K})(T_2 - 27°\text{C})$$

$$T_2 = 56.7°\text{C}$$

Discussion Note that we could also solve this problem by determining the boundary work and the internal energy change rather than the enthalpy change.