Name: SID: Discussion Section:

Chemical Engineering 141: Thermodynamics – Spring 2012

Thursday, February 23, 2011

Midterm 1 – 80 minutes – 115 points total
Use of phone devices is not permitted

Return your equation sheet with the exam

1. (15 points) Consider 1 mole of an ideal gas with constant heat capacities. For each of the following processes, deduce the signs for the quantities or changes in properties between initial and final states. W is defined as work done on the system by the surroundings. Indicate (0): no change, (+): positive change, or (-): negative change.

Process	ΔΤ	ΔΡ	ΔV	Q	W	ΔU	ΔΗ	ΔS
Reversible Isothermal Expansion	0	-	+	+	-	0	0	+
Reversible Constant-Volume Heating	+	+	0	+	0	+	+	+

2. (35 points) Consider an ideal gas with the following initial conditions:

$$P_i = 1 bar$$

$$V_i^t = 15 m^3$$

$$n = 500 mol$$

Also, throughout the entire problem, assume constant heat capacities, $c_p = 5/2R$ and $c_v = 3/2R$.

- a) (15 points) Calculate heat absorbed (Q), and work done (W) by system (W), as well as ΔU^t (all in units of kJ) for each of the subsequent reversible steps 1, 2, and 3.
 - 1. Adiabatic compression to 2 bars
 - 2. Constant pressure cooling to initial temperature
 - 3. Isothermal compression to 10 bars

(1)

Adiabatic compression

In a reversible adiabatic process involving an ideal gas, the following is true.

$$PV^{\gamma} = constant$$

$$\gamma = \frac{c_p}{c_v} = \frac{\frac{5}{2}R}{\frac{3}{3}R} = \frac{5}{3}$$

So,

$$\frac{P_i}{P_1} = \left(\frac{V_1}{V_i}\right)^{\gamma}$$

$$V_1 = \left(\frac{V_i^{\gamma}}{P_1}P_i\right)^{\frac{1}{\gamma}} = \left(\frac{\left(\frac{15 \ m^3}{500 \ mol}\right)^{\frac{5}{3}}}{2 \ bar} * 1bar\right)^{\frac{3}{5}} = 0.019793 \frac{m^3}{mol}$$

And also, with an adiabatic process,

$$TV^{\gamma-1} = constant$$

And (ideal gas)

$$T_i = \frac{P_i V_i}{R} = \frac{1 \ bar * 15 \ m^3}{8.314 * 10^{-5} bar \frac{m^3}{mol \ K} * 500 \ mol} = 360.84 \ K$$

So,

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$$T_1 = T_i * \left(\frac{V_i}{V_1}\right)^{\gamma - 1} = 360.84K * \left(\frac{0.03 \frac{m^3}{mol}}{0.019793 \frac{m^3}{mol}}\right)^{\frac{2}{3}} = 476.12$$

And thus, (W=work done by the system)

$$dU = \delta Q + \delta W$$

$$dU = \delta W$$

$$dU = c_V dT$$

$$\Delta U = \frac{3}{2}R \cdot (476.12 - 360.84)K = 1437.657 \frac{J}{mol}$$

$$\Delta U^t = 1437.657 \frac{J}{mol} \cdot 500mol = 718.8 \ kJ$$

$$Q = 0 \ (adiabatic)$$

$$W = 1437.66 \frac{J}{mol} = 718.83 \ kJ$$

(2)

Constant pressure cooling to Ti

Volume changes according to ideal gas

$$V_2 = \frac{RT_i}{P_1} = \frac{8.314 * 10^{-5} \frac{bar \cdot m^3}{mol \ K} * 360.84 \ K}{2 \ bar} = 0.015 \frac{m^3}{mol}$$

Then

$$dU = c_v dT$$

$$\Delta U = \frac{3}{2}R * (360.84 - 476.12) = -1437.657 \frac{J}{mol}$$

$$\Delta U^t = -718.8 \, kJ$$

$$\delta W = -P dV$$

$$W = -2 \, bar * \left(0.015 \frac{m^3}{mol} - 0.019793 \frac{m^3}{mol} \right) = 958.6 \frac{J}{mol} = 479.3 \, kJ$$

$$Q = \Delta U - W = -1437.657 - 958.6 = -2396.3 \frac{J}{mol} = -1198.15 \, kJ$$

(3)

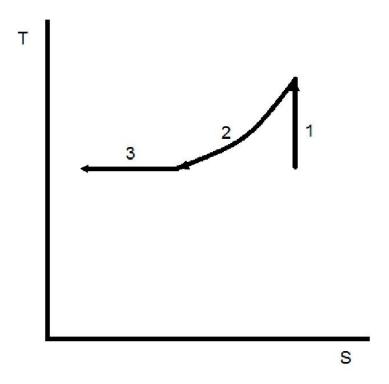
Isothermal Compression to 10 bars

$$\begin{split} &\Delta U^t = 0 \\ &\delta Q = -\delta W \\ &\delta W = -PdV = -Pd\left(\frac{RT}{P}\right) = \frac{RTP}{P^2}dP = \frac{RT}{P}dP \end{split}$$

$$W = RT \int_{2 \ bar}^{10 \ bar} \frac{1}{P} dP = R(360.84K) ln\left(\frac{10}{2}\right) = 4828.35 \frac{J}{mol} = 2414.175 \ kJ$$

$$Q = -4828.35 \frac{J}{mol} = -2414.175 \ kJ$$

b) (6 points) Draw the stepwise processes (a) on a T-S diagram. Label steps 1, 2, and 3.



c) (6 points) Calculate heat absorbed (Q) and work done (W) by system, as well as ΔU^t (all in units of kJ) for a single, reversible, isothermal process that takes the ideal gas from initial conditions to the conditions of step (3). How does this value compare to the total ΔU^t from part (a)?

Single isothermal process

Compress to ten bars

$$\Delta U = 0$$

$$\delta Q = -\delta W$$

$$W = RT \int_{1 \ bar}^{10 \ bar} \frac{1}{P} dP = R(360.84K) ln\left(\frac{10}{1}\right) = 6907.81 \frac{J}{mol} = 3453.905 \text{ kJ}$$

$$Q = -6907.81 \frac{J}{mol} = -3453.905 \text{ kJ}$$

Total for paths in part (a)

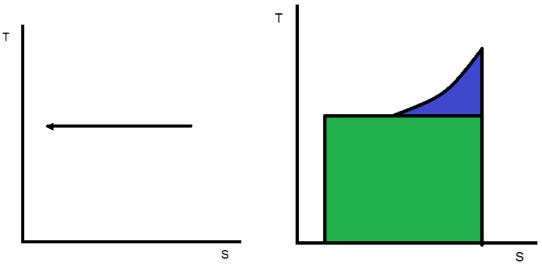
$$\Delta U^t = 0$$

Here we find that U^t in parts (a) and (b) are the same. This is due to 1) same initial and final conditions and also 2) U=f(T) and the process is isothermal. Q and W for the stepwise process and the single step process are different reflecting the path dependent nature of these properties. Q is the same value of W in both cases reflecting the first law of thermodynamics (U=Q-W).

d) (3 points) Draw this single step process (c) on a T-S diagram. Which process ((a) or (c)) requires more work? Depict this graphically.

Single Step Process

Comparison of the work of processes (a) and (c)



The stepwise process requires more work. Graphically, this is depicted as the negative area of the TS diagram. The comparison is shown below (supposing we shade the single step work in yellow and the stepwise in blue—recall the yellow+blue=green). We see the blue area represents the additional work required for the stepwise.

3. (30 points) Consider a rigid well-insulated storage tank with 100 m³ capacity (see figure). Initially (state 1), it contains 90 m³ liquid oleum, with the remaining space containing nitrogen at T_1 =300 K at P_1 =0.1 MPa. The oleum is transferred from this tank to another vessel by pressurizing the tank with nitrogen from a supply line where P_{in} =2 MPa and T_{in} =300 K.

Assumptions:

Treat nitrogen as an ideal gas and oleum as non-volatile liquid.

There is no energy transfer as heat from nitrogen to oleum in the tank.

Nitrogen does not dissolve in oleum and it does not leak outside when the outlet valve is closed.

Neglect potential energy/kinetic energy contributions.

 $\gamma = (c_p/c_v)=1.4$ for nitrogen.

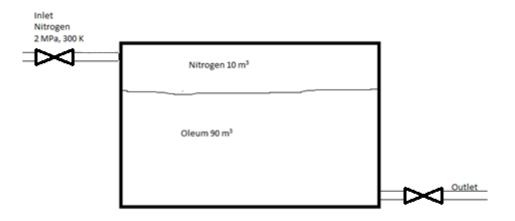


Figure:-Problem 2

a) (10 points) In the first step, the outlet valve is closed till the tank reaches a pressure of $P_2=2$ MPa (state 2). Show that

$$n_2T_2-n_1T_1 = \gamma T_{in}(n_2-n_1)$$

where n_1 and n_2 correspond to the number of moles of nitrogen in the tank in states 1 and 2 respectively.

Our system is the region above oleum occupied by nitrogen.

For this part, $\dot{m}_{\rm out}$ =0, also no KE/PE effects.

Since total volume of nitrogen remains the same, \dot{W}_{s} = 0

Also, as there is no heat interaction of the system with oleum or tank, \dot{Q} = 0

The 1st law for open system (transient) gives

$$\frac{d(mU)}{dt} = \left[(H_{in} + \frac{u_{in}^2}{2} + gZ_{in})\dot{m}_{in} \right] - \left[(H_{out} + \frac{u_{out}^2}{2} + gZ_{out})\dot{m}_{out} \right] + \dot{Q} + \dot{W},$$

$$\frac{d(mU)}{dt} = H_{in} \frac{dm_{in}}{dt}$$

where we identify that $\dot{m}_{in} = \frac{dm_{in}}{dt}$

We then cancel out the dt terms and are left with

$$d(mU) = H_{in}dm_{in}$$

During this process, the mass of gas inside the tank (m) and the temperature of the gas inside the tank (hence U) changes. So we write the left hand side of the equation as:

$$d(mU) = mdU + Udm$$

Doing a mass balance on the tank yields the following:

$$dm_{in} = dm$$

Hence we can combine the equations to

$$mdU + Udm = H_{in}dm$$

or
$$mdU = (H_{in} - U)dm$$

or
$$\frac{dm}{m} = \frac{dU}{H_{in} - U}$$

Integration this between initial and final states:

$$\ln(m_2/m_1) = \ln \frac{H_{in} - U_1}{H_{in} - U_2}$$

$$\frac{m_2}{m_1} = \frac{H_{\rm in} - U_1}{H_{\rm in} - U_2}$$

Since number of moles n=m/M where M is the molecular weight

$$\frac{m_2}{m_1} = \frac{n_2}{n_1} = \frac{H_{\rm in} - U_1}{H_{\rm in} - U_2}$$

For H_{in} - U_1 = U_{in} + $P_{in}V_{in}$ - U_1

=
$$(U_{in}-U_1)+RT_{in}$$
 [$P_{in}V_{in}=RT_{in}$ for an ideal gas]

$$=C_v(T_{in}-T_1)+RT_{in}[U_{in}-U_1=C_v(T_{in}-T_1)]$$
 for an ideal gas only]

$$=(C_v+R)T_{in}-C_vT_1$$

$$=C_pT_{in}-C_vT_1$$
 [$C_p=C_v+R$ for an ideal gas only]

Similarly, it can be shown

$$H_{in}$$
- U_2 = C_pT_{in} - C_vT_2

The above method does not require the assumption that at T=0 K, U=0 for an ideal gas.

Putting this back in we get

$$\frac{n_2}{n_1} = \frac{C_p T_{in} - C_v T_1}{C_p T_{in} - C_v T_2}$$

$$n_2 (C_p T_{in} - C_v T_2) = n_1 (C_p T_{in} - C_v T_1)$$

$$(n_2 - n_1) C_p T_{in} = n_2 C_v T_2 - n_1 C_v T_1$$

$$(n_2 - n_1) \gamma T_{in} = n_2 T_2 - n_1 T_1 \quad (where \ \gamma = \frac{C_P}{C_V})$$

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b) (20 points) Assume that the temperature we obtain from part (a) is T_2 =412 K. Then, once a pressure of 2 MPa is reached, the outlet valve is opened to withdraw oleum while keeping the pressure inside the tank fixed at 2 MPa. Oleum discharges slowly from the tank at a constant mass flow rate. Calculate the temperature of nitrogen in the tank when all the oleum has been discharged and the tank contains only nitrogen.

Control Volume:- Gas space in the oleum tank which changes as oleum drains out. Here also

For this part, $\dot{m}_{\rm out}$ =0, also no KE/PE effects.

Also as no there is no heat interaction with of the system with oleum or tank, \dot{Q} =0

The 1st law for open system gives

$$\frac{d(mU)}{dt} = [(H_{\rm in} + \dot{\psi}_{\rm in}^2/2 + gz_{\rm in})\dot{m}_{\rm in}] - [(H_{\rm out} + u_{\rm out}^2/2 + gz_{\rm out})\dot{m}_{\rm out}] + \dot{\psi}_{\rm s}$$

$$\frac{d(mU)}{dt} = H_{\rm in} \frac{dm_{\rm in}}{dt} + \dot{W}_{\rm s}$$

 $d(mU) = H_{in}dm_{in} + \delta W_s$

d(mU)=mdU+Udm

$$\delta W_s = -PdV^t = -Pd(mV) = -PmdV - PVdm$$

From mass balance

dm_{in}=dm

Putting all these back into the energy equation

mdU+Udm= H_{in}dm-PmdV-PVdm

 $m(dU+PdV)=H_{in}dm-dm(U+PV)$

 $md(U+PV)=dm(H_{in}-U-PV)$ [P=constant for this process]

 $mdH=dm(H_{in}-H)$ [H=U+PV by definition]

or
$$\frac{dm}{m} = \frac{dU}{H_{\rm in}-H}$$

Integrating this between initial(2) and final(3) states

$$\ln(m_3/m_2) = \ln \frac{H_{in} - H_2}{H_{in} - H_3}$$

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$$\frac{m_3}{m_2} = \frac{H_{\rm in} - H_2}{H_{\rm in} - H_3}$$

Since number of moles n=m/M where M is the molecular weight

$$\frac{m_3}{m_2} = \frac{n_3}{n_2} = \frac{H_{\rm in} - H_2}{H_{\rm in} - H_3}$$

Since nitrogen is an ideal gas, n₃=P₃V₃^t/RT₃

$$n_2=P_2V_2^t/RT_2$$

Since P₃=P₂

$$\frac{T_2 V_{3^{t}}}{T_3 V_{2^{t}}} = \frac{H_{in} - H_2}{H_{in} - H_3}$$

Since nitrogen is an ideal gas, H_{in} - H_2 = $C_P(T_{in}$ - $T_2)$

Similarly H_{in} - H_3 = $C_P(T_{in}$ - $T_3)$

Substituting these in, we get

$$\frac{T_2 V_3^{\rm t}}{T_3 V_2^{\rm t}} = \frac{T_{\rm in} - T_2}{T_{\rm in} - T_3}$$

Rearranging, we get

$$T_3 = T_{in} \frac{1}{1 + \left[\left(\frac{T_{in}}{T_2} \right) - 1 \right] \left(\frac{V_2^t}{V_3^t} \right)}$$

Substituting T_{in} =300 K, T_2 =412 K, V_2^t =10 m³, V_3^t =100 m³, we get

 $T_3 = 308 \text{ K}$

4. (35 points) A chemical engineer at Dow has created a new refrigerant for use in industrial freezers. This refrigerant has properties that can accurately be described by the following equation of state at pressures greater than 0.1 bar:

$$P = \frac{RT}{V - b} + a$$

With:

$$a = 8.41 * 10^{-3} bar$$
 $b = 0.03713 L/mol$

Assume constant $C_{P. gas} = 35.5 \text{ J/(mol*K)}$

Please answer the following questions and list any assumptions made:

a) (2 points) What purposes do the "a" and "b" terms seek to capture in the above equation of state?

The "a" term seeks to capture intermolecular forces. In this case, the sign of the term indicates molecular repulsions

The "b" term seeks to capture the volume of the individual molecules so that they cannot occupy the same space.

b) (8 Points) The refrigeration equipment is only rated to withstand a pressure of 50 bar. At what temperature will the vapor pressure exceed that pressure given that the boiling point is 195 K at ambient pressure and the latent heat of vaporization is a constant at a value of 23.35 kJ/mol? (You may assume the vapor to be an ideal gas for ease of calculation in this step)

Assume:

Ideal gas and that $V^L << V^G$

From Clausius-Clapeyron:

$$\frac{d(\ln P^{sat})}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H^{vap}}{R}$$

$$\ln \left(\frac{P^{sat}}{P^{sat}}\right) = \frac{-\Delta H^{vap}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$T_2 = \left[\ln \left(\left(\frac{P^{sat}}{P^{sat}}\right)^{\frac{-R}{\Delta H^{vap}}}\right) + \frac{1}{T_1}\right]^{-1} = \left[\ln \left(\left(\frac{50}{1}\right)^{\frac{-8.314}{23350}}\right) + \frac{1}{195}\right]^{-1} = \frac{1}{267.7 K}$$

- c) (15 Points) In an explosion, which occurred upon mechanical failure of the refrigeration system, the liquid boiled at vapor-liquid equilibrium until it was a saturated vapor at 27 °C and 155 bar. It then underwent an isentropic expansion of a gas during an explosion into a vacuum.
 - (i) (6 Points) Derive the differential expression for change in pressure with respect to temperature during the isentropic expansion of a gas in terms of measurable properties.

From the triple product rule (or ds = ds(T,P)):

$$\left(\frac{\partial P}{\partial T}\right)_{S} = -\left(\frac{\partial S}{\partial T}\right)_{P} \left(\frac{\partial P}{\partial S}\right)_{T}$$

From definition of Cp:

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{Cp}{T}$$

From Maxwell's Relations:

$$\left(\frac{\partial P}{\partial S}\right)_T = -\left(\frac{\partial T}{\partial V}\right)_P$$

Therefore:

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{Cp}{T} \left(\frac{\partial T}{\partial V}\right)_P$$

And:

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{\partial}{\partial V} \left[\frac{(P-a)(V-b)}{R}\right]_P = \frac{(P-a)}{R}$$

Finally:

$$\left(\frac{\partial P}{\partial T}\right)_{S} = \frac{Cp(P-a)}{RT}$$

(ii) (4 Points) Determine the final temperature of the gas after expansion to 1 bar.

$$\left(\frac{\partial P}{\partial T}\right)_{c} = \frac{Cp(P-a)}{RT}$$

$$\frac{dP}{(P-a)} = \frac{Cp}{R} \frac{dT}{T}$$

$$ln \left(\frac{(P_f - a)}{(P_i - a)} \right)^{\frac{R}{Cp}} = ln \left(\frac{T_2}{T_1} \right)$$

$$T_2 = T_1 \left(\frac{(P_f - a)}{(P_i - a)} \right)^{\frac{R}{Cp}} = 300K \left(\frac{(1 - a)}{(155 - a)} \right)^{\frac{8.314}{35.5}} = 92.1 \text{ K}$$

(iii) (5 Points) Using the sign of the partial derivative derived in (i), draw the line of isentropic expansion on a P, T diagram (Label your plot for which areas are gas, liquid, and solid). Assume the solid expands upon melting when drawing the fusion curve.

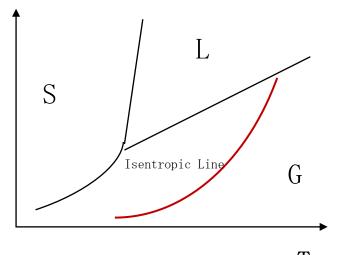
$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{Cp(P-a)}{RT}$$

Р

Since Cp, P, and T are required to be positive and P>a:

$$\left(\frac{\partial P}{\partial T}\right)_S>0$$

Also, due to expansion on melting, the slope of the fusion curve is positive (Clapeyron eqn)



d) Derive an expression for $C_p - C_v$ for this equation of state for the refrigerant for (i) the gas phase and (ii) as an incompressible fluid. (10 Points)

Discussion Section:

i) Below is one way to prove this mathematically:

From ds = ds(T,V):
$$ds = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

From definition of Cv:
$$ds = \frac{cv}{T}dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

From Maxwell's Relations:
$$ds = \frac{cv}{T}dT + \left(\frac{\partial P}{\partial T}\right)_V dV$$

Taking the Derivative:
$$\frac{\partial}{\partial T} \left[ds = \frac{cv}{T} dT + \left(\frac{\partial P}{\partial T} \right)_V dV \right]_P$$

$$\left(\frac{\partial S}{\partial T}\right)_{P} = \frac{Cv}{T} + \left(\frac{\partial P}{\partial T}\right)_{V} \left(\frac{\partial V}{\partial T}\right)_{P}$$

$$\frac{Cp}{T} = \frac{Cv}{T} + \left(\frac{\partial P}{\partial T}\right)_{V} \left(\frac{\partial V}{\partial T}\right)_{P}$$

Now:
$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$
 and $\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P-a}$

Therefore:
$$Cp = Cv + \left(\frac{RT}{V-b}\right)\left(\frac{R}{P-a}\right)$$

But remember the form of the EOS:

Therefore:
$$Cp - Cv = (P - a)\left(\frac{R}{P - a}\right) = R$$

ii) Incompressible

From the Triple Product Rule:

$$\left(\frac{\partial P}{\partial T}\right)_{V} = -\left(\frac{\partial P}{\partial V}\right)_{T} \left(\frac{\partial V}{\partial T}\right)_{P}$$

And for an incompressible fluid: $\left(\frac{\partial P}{\partial V}\right)_T=0$

Therefore:
$$Cp - Cv = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P = 0$$

Table A.1: Conversion Factors

Quantity	Conversion
Length	1 m = 100 cm = 3.28084(ft) = 39.3701(in)
Mass	$1 \text{ kg} = 10^3 \text{ g}$ = 2.20462(lb_{m})
Force	1 N = $\frac{1}{10}$ kg m s ⁻² = 10 ⁵ (dyne) = 0.224809(lb _f)
Pressure	1 bar = 10^5 kg m ⁻¹ s ⁻² = 10^5 N m ⁻² = 10^5 Pa = 10^2 kPa = 10^6 (dyne) cm ⁻² = 0.986923 (atm) = 14.5038 (psia) = 750.061 (torr)
Volume	1 m ³ = 10^6 cm ³ = 10^3 liters = $35.3147(\text{ft})^3$ = $264.172(\text{gal})$
Density	1 g cm ⁻³ = 10^3 kg m ⁻³ = $62.4278(lb_m)(ft)^{-3}$
Energy	$\begin{split} 1 J &= 1 \text{kg m}^2 \text{s}^{-2} = 1 \text{N m} \\ &= 1 \text{m}^3 \text{Pa} = 10^{-5} \text{m}^3 \text{bar} = 10 \text{cm}^3 \text{bar} \\ &= 9.86923 \text{cm}^3 (\text{atm}) \\ &= 10^7 (\text{dyne}) \text{cm} = 10^7 (\text{erg}) \\ &= 0.239006 (\text{cal}) \\ &= 5.12197 \times 10^{-3} (\text{ft})^3 (\text{psia}) = 0.737562 (\text{ft}) (\text{lb}_f) \\ &= 9.47831 \times 10^{-4} (\text{Btu}) = 2.77778 \times 10^{-7} \text{kWhr} \end{split}$
Power	I kW = 10^3 W = 10^3 kg m ² s ⁻³ = 10^3 J s ⁻¹ = 239.006 (cal) s ⁻¹ = 737.562 (ft)(Ib _f) s ⁻¹ = 0.94783 I(Btu) s ⁻¹ = 1.34102 (hp)

Table A.2: Values of the Universal Gas Constant

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\begin{split} R &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = 8.314 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1} \\ &= 83.14 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1} = 8,314 \text{ cm}^3 \text{ kPa mol}^{-1} \text{ K}^{-1} \\ &= 82.06 \text{ cm}^3 (\text{atm}) \text{ mol}^{-1} \text{ K}^{-1} = 62,356 \text{ cm}^3 (\text{torr}) \text{ mol}^{-1} \text{ K}^{-1} \\ &= 1.987 (\text{cal}) \text{ mol}^{-1} \text{ K}^{-1} = 1.986 (\text{Btu}) (\text{lb mole})^{-1} (\text{R})^{-1} \\ &= 0.7302 (\text{ft})^3 (\text{atm}) (\text{lb mol})^{-1} (\text{R})^{-1} = 10.73 (\text{ft})^3 (\text{psia}) (\text{lb mol})^{-1} (\text{R})^{-1} \\ &= 1,545 (\text{ft}) (\text{lb}_f) (\text{lb mol})^{-1} (\text{R})^{-1} \end{split}
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