Chemistry 342

First Exam ANSWERS
February 4, 2005
2:00 PM in C6 Lecture Center

Write all work you want graded in the spaces provided. Both the logical solution to the problem and the answer to the question are required. Final numerical values receive only small additional credit. What is required is an answer in terms of the original numerical data, including all numerical values and units of conversion factors. Use no intermediate calculated numbers, except where such numbers arise from answers to previous parts. The solution has to be worked out in the form of complete equations, with justification or basis for the use in the specific problem.

Example:

Solutions	
Step 1	$d\boldsymbol{w} = - p_{op} dV$ *definition* $d\boldsymbol{U} = C_V dT + (\partial \boldsymbol{U}/\partial V)_T \, dV$ Apply dV = 0 (constant volume) $\therefore \boldsymbol{w} = 0$ $\therefore d\boldsymbol{U} = C_V dT$ Apply $C_V = (3/2)R$ (given) integrate to $\Delta \boldsymbol{U} = \int C_V dT = (3/2)R\,[Tf - Ti]$ $\Delta \boldsymbol{U} = \boldsymbol{q} + \boldsymbol{w}$ First Law Rearrange and apply $\boldsymbol{w} = 0$ $\boldsymbol{q} = \Delta \boldsymbol{U} - 0$
Step 2	$d\boldsymbol{U} = C_V dT + (\partial \boldsymbol{U}/\partial V)_T \, dV$ Apply $dT = 0$ (constant temperature) Apply $(\partial \boldsymbol{U}/\partial V)_T = 0$ (ideal gas) $\therefore \Delta \boldsymbol{U} = 0 + 0$ $d\boldsymbol{w} = - p_{op} dV$ *definition* Apply $p_{op} = p_{gas}$ (reversible process) $p_{gas} = nRT/V$ (ideal gas) $\therefore \boldsymbol{w} = - \int p_{gas} \, dV = - \int nRT/V \, dV = - nRT \ln(Vf/Vi)$ $\Delta \boldsymbol{U} = \boldsymbol{q} + \boldsymbol{w}$ First Law Rearrange and apply $\Delta \boldsymbol{U} = 0$ and $\boldsymbol{w} = - nRT \ln(Vf/Vi)$ from above, $\therefore \boldsymbol{q} = + nRT \ln(Vf/Vi)$

Answers	Work, joules	Heat, joules
Step 1	0 J	(3/2)(8.3144)(273-172) J
Step 2	-8.3144(273) ln(1/2) J	8.3144(273) ln(1/2) J

POSSIBLY USEFUL INFO: 1 J = 1 kg m^{-2} s^{-2} $(p + n^2a/V^2)(V - nb) = nRT$

R = 8.31441 J mol^{-1} K^{-1} =1.98718 cal mol^{-1} K^{-1} =0.082057 L atm mol^{-1} K^{-1} 1 atm = 101325 Pa

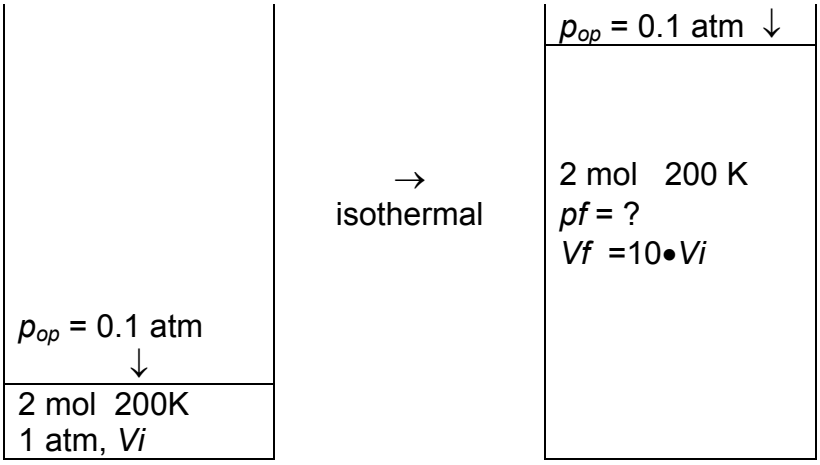
$(\partial \boldsymbol{U}/\partial V)_T = T(\partial p/\partial T)_V - p$ $(\partial \boldsymbol{H}/\partial p)_T = -T(\partial V/\partial T)_p + V$ $\mu_{JT} \equiv (\partial T/\partial p)_{\boldsymbol{H}}$ $(\partial \boldsymbol{H}/\partial p)_T = -C_p \mu_{JT}$

$C_p - C_V = \{p + (\partial \boldsymbol{U}/\partial V)_T\}(\partial V/\partial T)_p$

special case : $[T_f/T_i]^{Cv/R}\} = [V_i/V_f]$ only for ideal gas undergoing reversible adiabatic process

1. Two moles of a van der Waals gas undergoes isothermal expansion from 1 atm, 200 K to ten times its initial volume against a constant pressure of 0.1 atm. The parameters for this gas are:
a = 1.4 L^2 atm mol^{-2}, b = 0.39 L mol^{-1} ,
C_V = (5/2)R -0.370x10^{-3}T + 25.46x$10^{-7}T^2$ cal mol^{-1} K^{-1}.
Find the initial volume in liters, final pressure in atm, w, q, ΔU, ΔH in J

Space for a sketch (if desired)



Solutions	
initial volume	$(p_i + n^2a/V_i^2)(V_i - nb) = nRT_i$ Apply p_i = 1 atm, T_i = 200 K, a = 1.4 L^2 atm mol^{-2}, b = 0.39 L mol^{-1} $(1_i+2^2x1.4a/V_i^2)(V_i – 2x0.39) = 2x0.08205x200$ Solve for V_i
final pressure	$p = nRT/(V-nb) - n^2a/V^2$ Apply $T_f = T_i$ = 200 K Apply $V_f = 10V_i$ $p_f = 2x0.08205x200x(10V_i - 2x\ 0.39)^{-1} - 2^2x1.4[10V_i]^{-2}$ Apply V_i
w	$dw = - p_{op}dV$ $w = - p_{op}\int dV = -0.1\ [V_f - V_i]$ Apply $V_f = 10V_i$ $w = -0.1\ [10-1]\ V_i$ Apply V_i
q	$\Delta U = q + w$ First Law Rearrange to $q = \Delta U - w$ Apply ΔU and w from previous calculations

$\Delta \boldsymbol{U}$	$d\boldsymbol{U} = C_V dT + (\partial \boldsymbol{U}/\partial V)_T \, dV$ $(\partial U/\partial V)_T = T(\partial p/\partial T)_V - p$ given general eqn Rearrange eqn of state to get $p = nRT/(V\text{-}nb) - n^2a/V^2$ $(\partial p/\partial T)_V = nR/(V\text{-}nb)$ $(\partial U/\partial V)_T = nRT/(V\text{-}nb) - \{nRT/(V\text{-}nb) - n^2a/V^2\} = n^2a/V^2$ $\therefore d\boldsymbol{U} = C_V dT + [n^2a/V^2]dV$ Apply $dT = 0$ isothermal integrate $\Delta \boldsymbol{U} = 0 + n^2a \int V^{-2} \, dV$ to $\Delta \boldsymbol{U} = 2^2 x1.4x(-2)[V_f^{-1} - V_i^{-1}]$ Apply $V_f = 10V_i$ $\Delta \boldsymbol{U} = 2^2 x1.4x(-2)[10^{-1} - 1] V_i^{-1}$ Apply V_i
$\Delta \boldsymbol{H}$	$\boldsymbol{H} \equiv \boldsymbol{U} + pV$ *definition* apply definition of state function $\Delta \boldsymbol{H} = \Delta \boldsymbol{U} + p_f V_f - p_i V_i$ Apply $\Delta \boldsymbol{U} = 2^2 x1.4x(-2)[10^{-1} - 1] V_i^{-1}$ and $p_i = 1$ atm, $V_f = 10V_i$ $\Delta \boldsymbol{H} = 2^2 x1.4x(-2)[10^{-1} - 1] V_i^{-1} + p_f \, 10V_i - 1 \times V_i$ Apply p_f and V_i from previous calculations

	Answers	Final number	Units
initial volume	$(1_i + 2^2 x1.4a/V_i^2)(V_i - 2x0.39) = 2x0.08205x200$ Use ideal gas law to find V_{ideal} to see which correction is large enough to matter. $V_{ideal} = 32.823$, which leads to $2^2 x1.4/V_i^2 \approx .005$. Can use this. Thus, need only to leave $V_i - 2x0.39$ term in the eqn. to be solved.	$V_i = 33.5$ L	L
final pressure	$p_f = 2x0.08205x200x(10V_i - 2x0.39)^{-1} - 2^2 x1.4[10V_i]^{-2}$ Substitute V_i	$p_f = 0.0982$	atm
w	$w = -0.1[10\text{-}1] \, V_i \, x8.3144/0.08205$ Substitute V_i	- 3055	J
q	$q = \Delta \boldsymbol{U} - w$ do this after $\Delta \boldsymbol{U}$	+ 3085	J
$\Delta \boldsymbol{U}$	$\Delta \boldsymbol{U} = 2^2 x1.4x(-2)[10^{-1} - 1] V_i^{-1} x8.3144/0.08205$ do this before q	+30.5	J
$\Delta \boldsymbol{H}$	$\Delta \boldsymbol{H} = \{2^2 x1.4x(-2)[10^{-1} - 1] V_i^{-1} + p_f \, 10V_i - 1 \times V_i\} x8.3144/0.08205$	+30.5 -61.1 = -30.6	J

2. The compressibility factor for a gas at 20º C is described by this equation for pressures up to 10 atm:

$Z = 1 - 2.024\times10^{-2}\, p$. The following properties of this gas are also known:

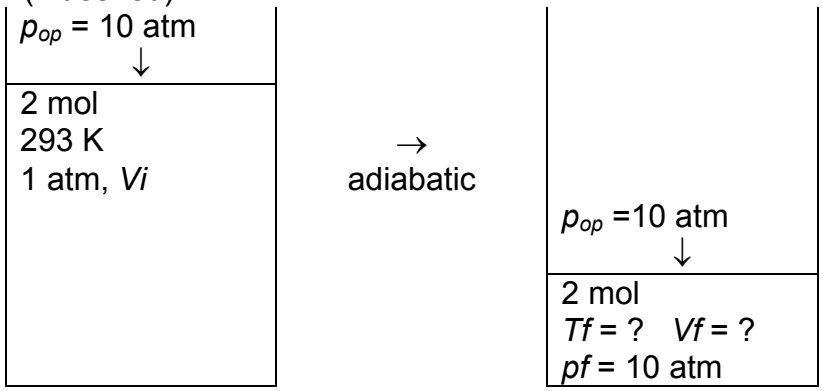
$C_V = 2.97 + 10.5\times10^{-3}\, T$ cal K^{-1} mol^{-1}

$C_p = 5.65 + 11.44\times10^{-3}\, T$ cal K^{-1} mol^{-1}

$(\partial U/\partial V)_T = 2\times10^{-3}$ cal L^{-1}

Two moles of a gas is compressed adiabatically in a single stage with a constant opposing pressure equal to 10 atm. Initially the gas is at 20º C and 1 atm pressure. The final pressure is 10 atm. Find the initial volume, final volume in liters, final temperature, w, q, ΔU, ΔH in J

Space for a sketch (if desired)

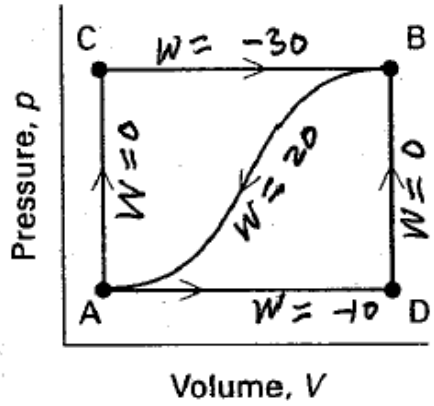


Solutions	
initial volume	$(pV/nRT) = 1 - 2.024\times10^{-2}\, p$, given, definition of Z Rearrange to $V = nRT[p^{-1} - 2.024\times10^{-2}]$ $V_i = nRT_i\,[p_i^{-1} - 2.024\times10^{-2}]$ Apply p_i = 1 atm, T_i = 293 K, n = 2 mol $V_i = 2\times0.08205\times293\,[1^{-1} - 2.024\times10^{-2}] = 2\times0.08205\times293\times0.980 = 47.12$ L
final volume	$V_f = nRT_f[p_f^{-1} - 2.024\times10^{-2}]$ Apply p_f = 10 atm, n = 2 mol $V_f = 2\times0.08205\times T_f\,[10^{-1} - 2.024\times10^{-2}]$ eqn (1) Requires another eqn in T_f and V_f [for which, see eqn (2) below]
final temperature	$dU = C_V dT + (\partial U/\partial V)_T\, dV$ $dU = dq + dw$ First Law $dq = 0$ adiabatic $dU = dw = -10\, dV$ $\therefore -10\, dV = C_V dT + (\partial U/\partial V)_T\, dV$ Apply $(\partial U/\partial V)_T = 2\times10^{-3}$ cal L^{-1} and $C_V = 2.97 + 10.5\times10^{-3}\, T$ cal K^{-1} mol^{-1} $-10\times(1.987/0.08205)\, dV = [2.97 + 10.5\times10^{-3}\, T]dT + 2\times10^{-3}\, dV$ Rearrange to $\{-10\times(1.987/0.08205) - 2\times10^{-3}\}\, dV = [2.97 + 10.5\times10^{-3}\, T]dT$ integrate $\{-10\times1.987/0.08205 - 2\times10^{-3}\}[V_f - V_i] = 2.97[T_f - T_i] + 10.5\times10^{-3}\times\tfrac{1}{2}[T_f^2 - T_i^2]$ Apply T_i = 293 , V_i = 47.12 L $\{-10\times1.987/0.08205 - 2\times10^{-3}\}[V_f - 47.12]$ $= 2.97[T_f - 293] + 10.5\times10^{-3}\times\tfrac{1}{2}[T_f^2 - 293^2]$ eqn (2) leaves both eqn (1) and eqn (2) in V_f and T_f as unknowns. It will be possible to get both by solving two equations in two unknowns.

w	$dw = -p_{op}dV$ Apply p_{op} = 10 atm $dw = -10\ dV$ $w = -10\ [V_f - V_i] \times 8.3144 / 0.08205$ Apply V_i = 47.12 L and V_f from above. $w = -10\ [V_f - 47.12] \times 8.3144 / 0.08205$
q	q = 0 definition of adiabatic
ΔU	$\Delta U = q + w$ First Law Apply q = 0 and w $\Delta U = 0\ -10\ [V_f - 47.12] \times 8.3144 / 0.08205$
ΔH	$H \equiv U + pV$ *definition* apply definition of state function $\Delta H = \Delta U + p_f V_f - p_i V_i$ Apply ΔU = $-10\ [V_f - 47.12] \times 8.3144 / 0.08205$ and p_i = 1, p_f = 10 atm V_i = 47.12 L $\Delta H = -10\ [V_f - 47.12] \times 8.3144 / 0.08205 + \{10V_f - 1 \times 47.12\} \times 8.3144 / 0.08205$ $\Delta H = 9 \times 47.12 \times 8.3144 / 0.08205$ J

	Answers	Final number	Units
initial volume	$2 \times 0.08205 \times 293 \times 0.980$	47.12	L
final volume	$V_f = 2 \times 0.08205 \times T_f\ [10^{-1} - 2.024 \times 10^{-2}]$ eqn (1) Solve 2 eqns in unknowns T_f and V_f		
final temperature	$\{-10 \times 1.987/0.08205 - 2 \times 10^{-3}\}[V_f - 47.12]$ $= 2.97[T_f - 293] + 10.5 \times 10^{-3} \times ½[T_f^2 - 293^2]$ eqn (2)		
w	$w = -10\ [V_f - 47.12] \times 8.3144 / 0.08205$		
q	$q = 0$		
ΔU	$\Delta U = -10\ [V_f - 47.12] \times 8.3144 / 0.08205$		
ΔH	$\Delta H = 9 \times 47.12 \times 8.3144 / 0.08205$ J		

3. When a system is taken from state A to state B along the path A→C→B in the figure below, 80 J of heat flows into the system and the system does 30 J of work.



(a) How much heat flows into the system along the path A→D→B if the work done is 10 J?
(b) When the system is returned from state B to A along the curved path, the work done on the system is 20 J. Does the system absorb or liberate heat, and how much?
(c) If $\boldsymbol{U}_D - \boldsymbol{U}_A = +40$ J, find the heat absorbed in each of the processes A→D and D→B

	Solution	Numerical Answer, J
(a)	$\Delta\boldsymbol{U} = q + w$ First Law $q_{ACB} = 80$ J, $w_{ACB} = -30$ J Given $\therefore \boldsymbol{U}_B - \boldsymbol{U}_A = q_{ACB} + w_{ACB} = 80-30 = q_{ADB} + w_{ADB} = q_{ADB} - 10$, $\boldsymbol{U}$ is state function	$q_{A\to D\to B} = +60$
(b)	$\Delta\boldsymbol{U} = q + w$ First Law $\boldsymbol{U}_A - \boldsymbol{U}_B = -50$ [from (a)] $= q_{B\circlearrowleft A} + w_{B\circlearrowleft A} = q_{B\circlearrowleft A} + 20$, $\boldsymbol{U}$ is state function	$q_{B\circlearrowleft A} = -70$ liberates heat to surrounds
(c)	$w_{DB} = -\int p_{op}dV = 0$ [dV=0] $w_{ADB} = -10$ [given in (a)] $= w_{AD} + w_{DB} = w_{AD} + 0$, leads to $w_{AD} = -10$ J $\Delta\boldsymbol{U} = q + w$ First Law $\boldsymbol{U}_D - \boldsymbol{U}_A = +40$ J [given] $= q_{AD} + w_{AD} = q_{AD} - 10$, leads to $q_{AD} = +50$ J $q_{ADB} = +60$ [from (a)] $= q_{AD} + q_{DB} = 50 + q_{DB}$, leads to $q_{DB} = +10$ J	$q_{A\to D} = +50$ $q_{D\to B} = +10$

4. A cylindrical container of fixed total volume is divided into three sections, S_1, S_2, and S_3. The sections S_1 and S_2 are separated by an adiabatic piston, whereas S_2 and S_3 are separated by a diathermic (heat conducting) piston. The pistons can slide along the walls of the cylinder without friction. Each section of the cylinder contains 1.00 mole of a perfect diatomic gas [$C_V = (5/2)R$]. Initially the gas pressure in all three sections is 1.00 atm and the temperature is 298 K. The gas in S_1 is heated slowly until the temperature of the gas in S_3 reaches 348 K. Find the final temperature, pressure, and volume, as well as the change in internal energy for each section. Determine the total energy supplied to the gas in S_1.

Space for a sketch (required)

	S_1	S_2	S_3
Initial:	$p_1 = 1$atm $T_1 = 298$ K	$p_2 = 1$atm $T_2 = 298$ K	$p_3 = 1$atm $T_3 = 298$ K
ideal:	$V_1 = ?=298R/1=24.4$ L	$V_2 = ?=298R/1=24.4$ L	$V_3 = ?=298R/1=24.4$ L

Solution:

Since fixed total volume, total work = 0, $w_1 + w_2 + w_3 = 0$ (1)

Since adiabatic piston between S_1 and S_2, $q_2 + q_3 = 0$ (2)

Since pistons are free to slide, then final $p_{f1} = p_{f2} = p_{f3} = p_f$

Since diathermic piston between S_2 and S_3, then T_{f2} is same as T_{f3} = 348 K

Since S_2 and S_3 are at same final p_f and T_f then $V_{f2} = V_{f3}$

What can we calculate?

$$dU = C_V dT + (\partial U/\partial V)_T dV$$

Apply $(\partial U/\partial V)_T = 0$ [ideal gas] and R = 1.987 cal mol^{-1} K^{-1} to Section S_2 and Section S_3:

$$\Delta U_2 = C_V [348 - 298] = (5/2)R[348 - 298] = 250 \text{ cal}$$

$$\Delta U_3 = C_V [348 - 298] = (5/2)R[348 - 298] = 250 \text{ cal}$$

First law: $\Delta U_2 = q_2 + w_2$ and $\Delta U_3 = q_3 + w_3$

But since $q_2 + q_3 = 0$ from (2) and $w_1 + w_2 + w_3 = 0$ from (1) then

$$w_1 = -(w_2 + w_3) = -(\Delta U_2 + \Delta U_3) = -(250+250) = -500 \text{ cal}$$

Ideal gases in S_2 and S_3 together went through an adiabatic reversible (infinitely slowly) compression brought about by expansion of S_1.

Therefore, $\ln\{ [T_{f2}/T_{i2}]^{Cv/R} \} = \ln [V_{i2}/V_{f2}]$ holds.

$$\ln\{ [348/298]^{5/2} \} = \ln [298R/V_{f2}] \text{, solve for } V_{f2} = 16.59 \text{ L} = V_{f3}$$

Ideal gas equation gives p_f from known T_{f2} and V_{f2}: $p_f = R\,(348)/V_{f2} = 1.72$ atm

We know also that fixed total volume is the same as total initial volume,

$$V_{f1} + 2V_{f2} = 3 \cdot R298/1$$

From V_{f2} =16.59 L, solve for V_{f1}: V_{f1} = 40.16 L

In S_1 we know the values p_f and V_{f1}, apply ideal gas law: $p_f V_{f1} = R\,(T_{f1})$

Solve for T_{f1} T_{f1} = 1.72 atm(40.16 L) /.082057 = 841.8 K

In S_1 can now apply First Law: $\Delta U_1 = C_V [T_{f1} - 298] = q_1 + w_1$

substituting values of T_{f1} and w_1: (5/2)R[841.8 - 298] = 2701.6 cal = q_1 - 500 cal ,

solve for q_1: q_1 = 3202 cal which is the total energy supplied to the gas in S_1.

Answers								
Section S_1			Section S_2			Section S_3		
p_{f1} =	1.72	atm	p_{f2} =	1.72	atm	p_{f3} =	1.72	atm
V_{f1} =	40.16	L	V_{f2} =	16.59	L	V_{f3} =	16.59	L
T_{f1} =	841.8	K	T_{f2} =	348	K	T_{f3} =	348	K
ΔU_1 =	2701.6	cal	ΔU_2 =	250	cal	ΔU_3 =	250	cal
Total energy supplied to the gas in Section S_1 =				3202	cal			

5.(a) The following data have been obtained for the density of a gas as a function of pressure at 10° C. find the molar mass (molecular weight) of the gas.

p, atm	0.68	2.72	8.14
ρ, g L^{-1}	1.29	5.25	16.31

Hint: the gas is not ideal but you can find the limit of ρ/p as the gas approaches ideality.

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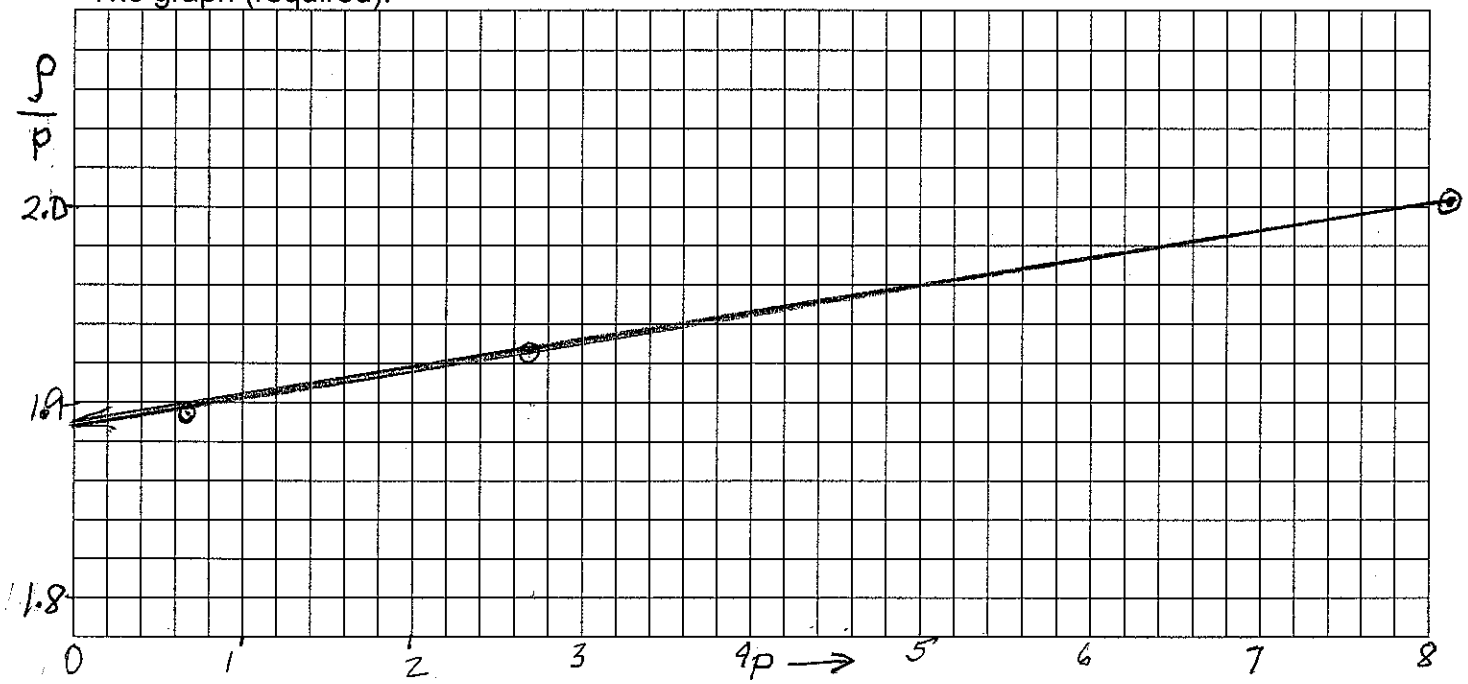
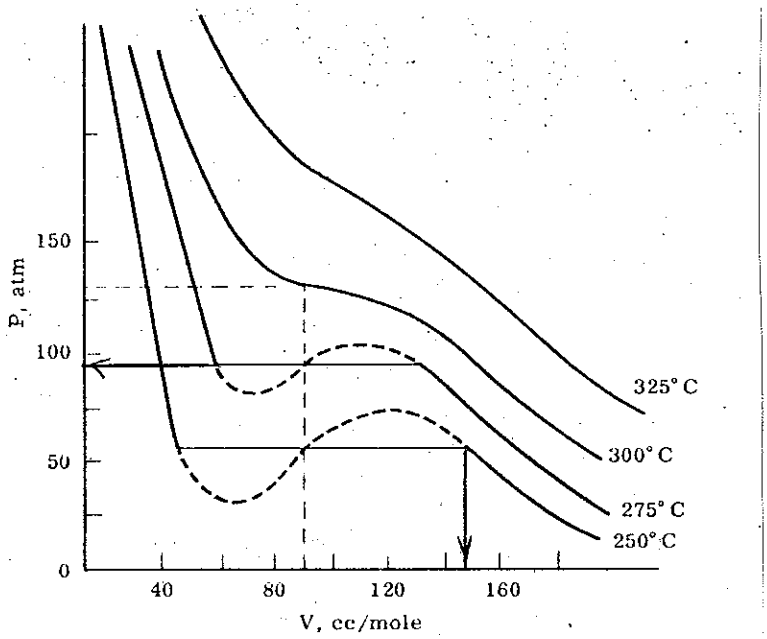
p, atm	0.68	2.72	8.14
ρ/p, g L^{-1} atm^{-1}	1.89_6	1.92_6	2.00_6

The graph (required):



Solution	**Answer**	**Final number**	**Units**
In the limit p→0, gas behaves like an ideal gas. From the graph, $(\rho/p)_{ideal} = 1.89_0$ g L^{-1} atm^{-1} pV = nRT = m/MRT M = (m/V)RT/p = $(\rho/p)_{ideal}$ RT	M = 1.890x0.08205x283	44.0	g mol^{-1}

5.(b) Given the *pV* plots for a gas in the figure below:



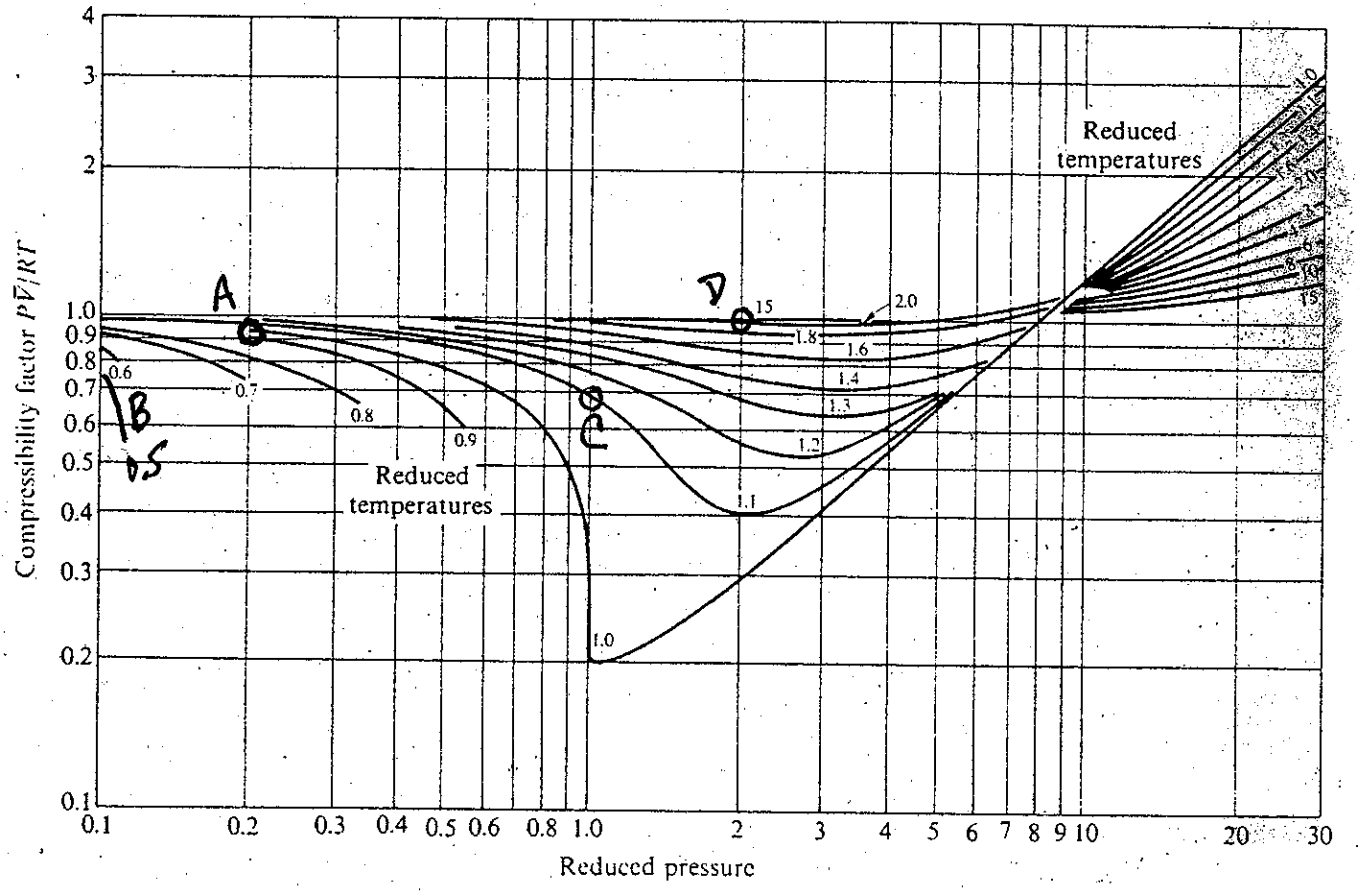
(a) What is the critical temperature of the gas?	300	°C
(b) What is the critical pressure of the gas?	130	atm
(c) A sample of the gas is collected in a flask at 325°C. As it is slowly cooled, it condenses at 250°C. What is the density of the sample?	1 mol ÷ 0.147 L	mol L^{-1}
(d) What is the vapor pressure in equilibrium with the liquid at 275°C?	95 read off	atm

(c) The critical temperature and pressure for several gases are shown below:

gas	T_c, K	p_c, atm	T_r	p_r	Z
A	300	50	1.0	0.2	0.95
B	600	40	0.5	0.25	≤ 0.2
C	280	10	1.07	1.0	0.7
D	20	5	15.	2.0	1.0

Consult the figure on the next page and answer these questions based on it

	Solution and Reasoning	Answer choose one
(a) Which gas is most nearly ideal in behavior at 300 K and 10 atm?	Z closest to 1.0 is D	A B C **(D)**
(b) Which is the least ideal	Z most different from 1.0 is B	A **(B)** C D


Compressibility factor $P\bar{V}/RT$
Reduced pressure
Reduced temperatures
Reduced temperatures
A
B
C
D
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.6
1.8
2.0
15