Assume all gases are perfect and that the temperature is 298 K unless stated otherwise.

2. Suppose that 3.0 mmol of $N_2(g)$ occupies 36 cm^3 at 300 K and expands to 60 cm^3. Calculate ΔG for the process.

3. The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression $\Delta G/J = -85.40 + 36.5(T/K)$. Calculate the value of ΔS for the process.

4. When the pressure on a 35-g sample of a liquid was increased isothermally from 1 atm to 3000 atm, the Gibbs energy increased by 12 kJ. Calculate the density of the liquid.

5. When 2.00 mol of a gas at 330 K and 3.50 atm is subjected to isothermal compression, its entropy decreases by 25.0 $J\,K^{-1}$. Calculate the final pressure of the gas and ΔG for the compression.

6. Calculate the change in chemical potential of a perfect gas that is compressed isothermally from 1.8 atm to 29.5 atm at 40°C.

9. Estimate the change in the Gibbs energy of 1.0 L of benzene when the pressure acting on it is increased from 1.0 atm to 100 atm.

10. Calculate the change in the molar Gibbs energy of hydrogen gas when it is compressed isothermally from 1.0 atm to 100.0 atm at 298 K.

11. The molar Helmholtz energy of a certain gas is given by:

$$A = -\frac{a}{V_m} - RT\ln(V_m - b) + f(T)$$

where a and b are constants and $f(T)$ is a function of temperature only. Obtain the equation of state of the gas.

Assume all gases are perfect and that the temperature is 298 K unless stated otherwise.

2. Suppose that 3.0 mmol of N_2(g) occupies 36 cm^3 at 300 K and expands to 60 cm^3. Calculate ΔG for the process.

2. We need $\mathbf{G}$. Start with the definition

$$\mathbf{G} \equiv \mathbf{H} - T\mathbf{S} \qquad \mathbf{H} \equiv \mathbf{U} + pV$$

$$\therefore \quad \mathrm{d}\mathbf{G} = \mathrm{d}\mathbf{U} + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}\mathbf{S} - \mathbf{S}\mathrm{d}T$$

Now let us get rid of some terms above.

First Law says $\mathrm{d}\mathbf{U} = \eth q + \eth W$

Second law says $T\mathrm{d}\mathbf{S} = \eth q_{rev}$

For a reversible change,

$\eth W = -p_{op}\mathrm{d}V$ turns into $-p\mathrm{d}V$

$$\therefore \quad \mathrm{d}\mathbf{U} = T\mathrm{d}\mathbf{S} - p\mathrm{d}V$$

substitute into $\mathrm{d}\mathbf{G}$ to get

$$\boxed{\mathrm{d}\mathbf{G} = V\mathrm{d}p - \mathbf{S}\mathrm{d}T}$$

Now we are ready:

isothermal $\mathrm{d}T = 0$ leads to $\mathrm{d}\mathbf{G} = V\mathrm{d}p$

ideal gas $V = nRT/p$ leads to

Therefore $\int \mathrm{d}\mathbf{G} = \int V\mathrm{d}p = \int nRT\mathrm{d}p/p$

isothermal leads to $\int \mathrm{d}\mathbf{G} = nRT \ln p_f/p_i$

$p_f = nRT/V_f \quad p_i = nRT/V_i$ divide one eqn. by the other to get $p_f/p_i = V_i/V_f = 36/60$

$$\Delta\mathbf{G} = 3\times10^{-3}\,\mathrm{mol}\times 8.3144\ \mathrm{J\ K^{-1}mol^{-1}} \times 300\ \mathrm{K} \times \ln 36/60 = -3.8\ \mathrm{J}$$

3. The change in the Gibbs energy of a certain constant-pressure process was found to fit the expression $\Delta G/\mathrm{J} = -85.40 + 36.5(T/\mathrm{K})$. Calculate the value of ΔS for the process.

3. We need ***G*** and ***S***. Start with
definitions $\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S}$ $\qquad \boldsymbol{H} \equiv \boldsymbol{U} + pV$

$\therefore\ \mathrm{d}\boldsymbol{G} = \mathrm{d}\boldsymbol{U} + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}\boldsymbol{S} - \boldsymbol{S}\mathrm{d}T$

Now let us get rid of some terms above.

First Law says $\qquad \mathrm{d}\boldsymbol{U} = \text{đ}q + \text{đ}W$

Second law says $\quad T\mathrm{d}\boldsymbol{S} = \text{đ}q_{rev}$

For a reversible change,

$\text{đ}W = -p_{op}\mathrm{d}V$ $\qquad$ turns into $-p\mathrm{d}V$

$\therefore \qquad \mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V$

substitute into d***G*** to get

$$\boxed{\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T}$$

We are ready: constant pressure, dp = 0

$\therefore \mathrm{d}\boldsymbol{G} = \quad -\boldsymbol{S}\mathrm{d}T$

$(\partial\boldsymbol{G}/\partial T)_p = -\boldsymbol{S}$

$(\partial\boldsymbol{G}_f/\partial T)_p = -\boldsymbol{S}_f \qquad (\partial\boldsymbol{G}_i/\partial T)_p = -\boldsymbol{S}_i$

$\Delta\boldsymbol{S} = \boldsymbol{S}_f - \boldsymbol{S}_i \quad = -\{(\partial\boldsymbol{G}_f/\partial T)_p - (\partial\boldsymbol{G}_i/\partial T)_p\}$

$\qquad\qquad\qquad\quad = -(\partial\Delta\boldsymbol{G}/\partial T)_p$

Given $\Delta\boldsymbol{G} = -85.40 + 36.5(T/K)$

$(\partial\Delta\boldsymbol{G}/\partial T)_p = +\ 36.5\ \mathrm{J\ K^{-1}}$

$\Delta\boldsymbol{S} = -\ 36.5\ \mathrm{J\ K^{-1}}$

4. When the pressure on a 35-g sample of a liquid was increased isothermally from 1 atm to 3000 atm, the Gibbs energy increased by 12 kJ. Calculate the density of the liquid.

4. We need $\boldsymbol{G}$. Start with definitions

$$\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S} \qquad\qquad \boldsymbol{H} \equiv \boldsymbol{U} + pV$$

$$\therefore \quad \mathrm{d}\boldsymbol{G} = \mathrm{d}\boldsymbol{U} + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}\boldsymbol{S} - \boldsymbol{S}\mathrm{d}T$$

Now let us get rid of some terms above.

First Law says $\mathrm{d}\boldsymbol{U} = \eth q + \eth W$

Second law says $T\mathrm{d}\boldsymbol{S} = \eth q_{rev}$

For a reversible change,

$\eth W = -p_{op}\mathrm{d}V$ turns into $-p\mathrm{d}V$

$$\therefore \quad \mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V$$

substitute into $\mathrm{d}\boldsymbol{G}$ to get

$$\boxed{\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T}$$

Now we are ready:

(isothermal) $\mathrm{d}T = 0$ leads to $\mathrm{d}\boldsymbol{G} = V\mathrm{d}p$

$$\int \mathrm{d}\boldsymbol{G} = \int V\mathrm{d}p$$

For a liquid V is essentially independent of pressure $\therefore \int \mathrm{d}\boldsymbol{G} = V\int \mathrm{d}p = V(p_f - p_i)$

$$\Delta\boldsymbol{G} = V(3000 - 1) \text{ L atm}$$

$12 \times 10^3 \text{ J} \times \{0.082056 \text{ L atm} / 8.3144 \text{ J}\}$

$= V(3000 - 1)$. Solve for V, $V = .0395\text{L}$

density $= m/V = 35/\ .0395 \text{ L} = 886.3 \text{ g/L}$

5. When 2.00 mol of a gas at 330 K and 3.50 atm is subjected to isothermal compression, its entropy decreases by 25.0 J K^{-1}. Calculate the final pressure of the gas and ΔG for the compression.

5. To do this problem, we need to know how ***S*** and ***G*** change with *p*.

$$\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S} \qquad \boldsymbol{H} \equiv \boldsymbol{U} + pV$$

$\therefore \quad \mathrm{d}\boldsymbol{G} = \mathrm{d}\boldsymbol{U} + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}\boldsymbol{S} - \boldsymbol{S}\mathrm{d}T$

Now let us get rid of some terms above.

First Law says $\quad \mathrm{d}\boldsymbol{U} = \eth q + \eth W$

Second law says $\quad T\mathrm{d}\boldsymbol{S} = \eth q_{rev}$

For a reversible change,

$\eth W = -p_{op}\mathrm{d}V \quad$ turns into $-p\mathrm{d}V$

$\therefore \quad \mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V$

substitute into d***G*** to get

$$\boxed{\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T}$$

d***G*** is an exact differential, therefore the mixed derivatives are equal:

$(\partial V/\partial T)_p = -(\partial \boldsymbol{S}/\partial p)_T$

$$\boxed{\mathrm{d}\boldsymbol{S} = (1/T)C_p\,\mathrm{d}T - (\partial V/\partial T)_p\,\mathrm{d}p \quad \textit{general}}$$

Now we are ready:

isothermal $\quad \mathrm{d}T = 0$ leads to

$\mathrm{d}\boldsymbol{S} = -(\partial V/\partial T)_p\,\mathrm{d}p$

$\int d\boldsymbol{S} = \int -(\partial V/\partial T)_p \, dp$

ideal gas $pV = nRT$ leads to $V = nRT/p$

$(\partial V/\partial T)_p = nR/p$

$\Delta \boldsymbol{S} = \int d\boldsymbol{S} = \int -nR \, dp/p = -nR \ln(p_f/p_i)$

$- 25 \text{ J K}^{-1} =$

$-2 \text{ mol} \times 8.3144 \text{ J K}^{-1}\text{mol}^{-1} \ln(p_f/3.5)$

Solve for p_f, $p_f = 15.7$ atm

From $d\boldsymbol{G} = V dp - \boldsymbol{S} dT$

$\int d\boldsymbol{G} = \int V dp$ when isothermal

and ideal gas eqn $V = nRT/p$ leads to:

$$\Delta \boldsymbol{G} = \int nRT dp/p$$

isothermal leads to $\Delta \boldsymbol{G} = nRT \ln p_f/p_i$

$\Delta \boldsymbol{G} = -\text{T}\Delta \boldsymbol{S} = - 330 \text{ K} \times \{-25 \text{ J K}^{-1}\}$

$= + 8.25 \text{ kJ}$

Note

$\Delta \boldsymbol{G}_T = \Delta \boldsymbol{H} - \text{T}\Delta \boldsymbol{S}$

ideal gas $(\partial \boldsymbol{H}/\partial p)_T = 0$, and $dT = 0$ gives

$\Delta \boldsymbol{H} = 0$ also leads to

$\Delta \boldsymbol{G}_T = -\text{T}\Delta \boldsymbol{S}$ for this problem.

6. Calculate the change in chemical potential of a perfect gas that is compressed isothermally from 1.8 atm to 29.5 atm at 40°C.

6. Chemical potential is Gibbs energy per mole, so we need $\boldsymbol{G}$:

$\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S}$ $\qquad\qquad$ $\boldsymbol{H} \equiv \boldsymbol{U} + pV$

$\therefore\quad \mathrm{d}\boldsymbol{G} = \mathrm{d}\boldsymbol{U} + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}\boldsymbol{S} - \boldsymbol{S}\mathrm{d}T$

First Law says $\qquad \mathrm{d}\boldsymbol{U} = \text{đ}q + \text{đ}W$

Second law says $\quad T\mathrm{d}\boldsymbol{S} = \text{đ}q_{rev}$

For a reversible change,

$\text{đ}W = -p_{op}\mathrm{d}V$ $\qquad$ turns into $-p\mathrm{d}V$

$\therefore\qquad \mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V$

substitute into $\mathrm{d}\boldsymbol{G}$ to get

$$\boxed{\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T}$$

isothermal, at T, $\quad \int \mathrm{d}\boldsymbol{G} = \int V\mathrm{d}p$

$$\boldsymbol{G}_f(T) = \boldsymbol{G}_i(T) + \int_{p1}^{p2} V\,dp.$$

For an ideal gas

$$\boldsymbol{G}_f(T) = \boldsymbol{G}_i(T) + \int_{1}^{p} \frac{nRT}{p}\,dp\,.$$

Define the free energy per mole

(***the chemical potential,*** μ):

$$\mu_f\,(T) = \mu_i\,(T) + RT\ln\frac{p_2}{p_1} \quad \text{(ideal gas)}$$

$$\Delta\mu(T) = +RT \ln \frac{p_2}{p_1}$$

$= 8.3144\ \mathrm{J\ K^{-1} mol^{-1}} \times 313\ \mathrm{K} \times \ln(29.5/1.8)$

$= +7.3\ \mathrm{kJ\ mol^{-1}}$

9. Estimate the change in the Gibbs energy of 1.0 L of benzene when the pressure acting on it is increased from 1.0 atm to 100 atm.

9. We need ***G***. Start with definition

$\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S}$ $\qquad\qquad \boldsymbol{H} \equiv \boldsymbol{U} + pV$

$\therefore \quad \mathrm{d}\boldsymbol{G} = \mathrm{d}\boldsymbol{U} + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}\boldsymbol{S} - \boldsymbol{S}\mathrm{d}T$

Now let us get rid of some terms above.

First Law says $\qquad \mathrm{d}\boldsymbol{U} = \eth q + \eth W$

Second law says $\quad T\mathrm{d}\boldsymbol{S} = \eth q_{rev}$

For a reversible change,

$\eth W = -p_{op}\mathrm{d}V$ $\qquad$ turns into $-p\mathrm{d}V$

$\therefore \qquad \mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V$

substitute into d***G*** to get

$$\boxed{\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T}$$

Now we are ready: $\quad$ dT=0 (isothermal),

at T, $\int \mathrm{d}\boldsymbol{G} = \int V\mathrm{d}p$

$$\Delta \boldsymbol{G}(T) = \int_{p1}^{p2} V\,dp = V(p_2 - p_1)$$

= 1 L(100-1) atm = 99 L atm

= 99 L atm ×{8.3144 J /0.082056 L atm }

= 10 kJ

10. Calculate the change in the molar Gibbs energy of hydrogen gas when it is compressed isothermally from 1.0 atm to 100.0 atm at 298 K.

10. We need $\boldsymbol{G}$. Start with definition

$$\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S} \qquad \boldsymbol{H} \equiv \boldsymbol{U} + pV$$

$$\therefore \quad \mathrm{d}\boldsymbol{G} = \mathrm{d}\boldsymbol{U} + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}\boldsymbol{S} - \boldsymbol{S}\mathrm{d}T$$

Now let us get rid of some terms above.

First Law says $\mathrm{d}\boldsymbol{U} = \text{ð}q + \text{ð}W$

Second law says $T\mathrm{d}\boldsymbol{S} = \text{ð}q_{rev}$

For a reversible change,

$\text{ð}W = -p_{op}\mathrm{d}V$ turns into $-p\mathrm{d}V$

$$\therefore \quad \mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V$$

substitute into $\mathrm{d}\boldsymbol{G}$ to get

$$\boxed{\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T}$$

$\int \mathrm{d}\boldsymbol{G} = \int V\mathrm{d}p$ when isothermal ($\mathrm{d}T = 0$)
and ideal gas $V = nRT/p$ leads to:

$$\Delta\boldsymbol{G} = \int nRT\mathrm{d}p/p$$

isothermal leads to $\Delta\boldsymbol{G} = nRT \ln p_f/p_i$

$$\Delta\boldsymbol{G} = 1\ \text{mol} \times 8.3144\ \text{J K}^{-1}\text{mol}^{-1} \times 298\ \text{K} \times \ln(100/1) = +11\ \text{kJ mol}^{-1}$$

11. The molar Helmholtz energy of a certain gas is given by:

$$A = -\frac{a}{V_\mathrm{m}} - RT\ln(V_\mathrm{m} - b) + f(T)$$

where a and b are constants and $f(T)$ is a function of temperature only. Obtain the equation of state of the gas.

11. We need $\boldsymbol{A}$. Start with definition

$\boldsymbol{A} \equiv \boldsymbol{U} - T\boldsymbol{S}$ $\quad\quad$ $\mathrm{d}\boldsymbol{A} = \mathrm{d}\boldsymbol{U} - T\mathrm{d}\boldsymbol{S} - \boldsymbol{S}\mathrm{d}T$

Now let us get rid of some terms above.

First Law says $\quad\quad$ $\mathrm{d}\boldsymbol{U} = \eth q + \eth W$

Second law says $\quad$ $T\mathrm{d}\boldsymbol{S} = \eth q_{rev}$

For a reversible change,

$\eth W = -p_{op}\mathrm{d}V$ $\quad\quad$ turns into $-p\mathrm{d}V$

$\therefore \quad\quad \mathrm{d}\boldsymbol{U} = T\mathrm{d}\boldsymbol{S} - p\mathrm{d}V$

substitute into $\mathrm{d}\boldsymbol{A}$ to get

$$\boxed{\mathrm{d}\boldsymbol{A} = -p\mathrm{d}V - \boldsymbol{S}\mathrm{d}T}$$

What we need is an expression for p

$(\partial \boldsymbol{A}/\partial V)_T = -p$

This allows us to take from

$$A = -\frac{a}{V_{\mathrm{m}}} - RT\ln(V_{\mathrm{m}} - b) + f(T)$$

the derivative of the expression with respect to V:

$-p = (\partial \boldsymbol{A}/\partial V)_T = a/V^2 - RT\{1/(V-b)\}$

$p = -a/V^2 + RT\{1/(V-b)\}$

is the equation of state.

2. Calculate the equilibrium pressure for the conversion of graphite to diamond at 25°C. The densities of graphite and diamond may be taken to be 2.55 and 3.51 g cm^{-3}, respectively, independent of pressure.

$\Delta_f H^{\ominus}$ (diamond) = 0.4532 kcal mol^{-1}

$S^{\ominus}$(298 K)
= 0.5829 cal K^{-1} mol^{-1} for diamond
= 1.3609 cal K^{-1} mol^{-1} for graphite

5. Recognizing that the Gibbs free energy of fusion of ice at 0°C and 1 atm is equal to zero, and assuming the heat capacities of ice and supercooled water to be constant, derive by integration of the Gibbs-Helmholtz equation an expression for the Gibbs free energy of fusion of ice as a function of temperature. Also derive expressions for $\Delta_{fus}H$ and $\Delta_{fus}S$ as functions of temperature. If the specific heat of fusion of ice at 0°C and 1 atm is 79.7 cal g^{-1} and the specific heat capacities of ice and water are 0.48 and 1.00 cal K^{-1} g^{-1} respectively, what are the molar values for $\Delta_{fus}G$, $\Delta_{fus}H$, and $\Delta_{fus}S$ at -3°C?

EXAMPLE: **2.** Calculate the equilibrium pressure for the conversion of graphite to diamond at 25°C. The densities of graphite and diamond may be taken to be 2.55 and 3.51 g cm^{-3}, respectively, independent of pressure.

$\Delta_f H^{\ominus}$ (diamond) = 0.4532 kcal mol^{-1}

	$S^{\ominus}$(298 K) cal K^{-1} mol^{-1}
diamond	0.5829
graphite	1.3609

Question:

graphite(298 K, p) → diamond(298 K, p)
Find p at equilibrium.

Solution:

graphite(298, 1) → diamond(298, 1) (a)
graphite(298, 1) → graphite(298, p) (b)
diamond(298, 1)→ diamond(298, p) (c)
(a) -(b) +(c) =
graphite(298 K, p) → diamond(298 K, p)

Given for step (a):

graphite $\rightarrow$ diamond $\Delta_f \boldsymbol{H}^{\ominus} = 0.4532$

(298 K, 1 bar) (298, 1 bar) kcal mol^{-1}

$\boldsymbol{G} \equiv \boldsymbol{H} - T\boldsymbol{S}$

At constant $T = 298$ K, $\mathrm{d}T = 0$,

$\therefore \Delta \boldsymbol{G}_T = \Delta \boldsymbol{H} - T\Delta \boldsymbol{S}$ and

$\Delta \boldsymbol{G}^{\ominus} = \Delta \boldsymbol{H}^{\ominus} - T\Delta \boldsymbol{S}^{\ominus}$

$\Delta \boldsymbol{G}_a^{\ominus} = 453.2$ cal

-298 K $(0.5829 - 1.3609)$ cal K^{-1} mol^{-1}

$= 685$ cal

For (b) and (c):

As already derived in previous example,

$\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T \quad \mathrm{d}T = 0$

$\int \mathrm{d}\boldsymbol{G} = \int V\mathrm{d}p = V \int \mathrm{d}p$ since densities are given as independent of pressure.

$\Delta \boldsymbol{G}_b = (12/2.55)\times 10^{-3}$ L $[p - 1]$

$\Delta \boldsymbol{G}_c = (12/3.51)\times 10^{-3}$ L $[p - 1]$

Since p is the pressure at which the two phases are at equilibrium, $\Delta \boldsymbol{G}(p) = 0$.

$0 = \Delta \boldsymbol{G}_a - \Delta \boldsymbol{G}_b + \Delta \boldsymbol{G}_c$

$$0 = 685 + \{-(12/2.55) + (12/3.51)\} \times 10^{-3} (\boldsymbol{p} - 1) \times (1.987 \text{ cal})/(8.3144 \times 10^{-2} \text{ L bar})$$

Solve for ***p***

$p = 22269$ bar

EXAMPLE:

5. Recognizing that the Gibbs free energy of fusion of ice at 0°C and 1 atm is equal to zero, and assuming the heat capacities of ice and supercooled water to be constant, derive by integration of the Gibbs-Helmholtz equation an expression for the Gibbs free energy of fusion of ice as a function of temperature. Also derive expressions for $\Delta_{fus}\boldsymbol{H}$ and $\Delta_{fus}\boldsymbol{S}$ as functions of temperature. If the specific heat of fusion of ice at 0°C and 1 atm is 79.7 cal g^{-1} and the specific heat capacities of ice and water are 0.48 and 1.00 cal K^{-1} g^{-1} respectively, what are the molar values for $\Delta_{fus}\boldsymbol{G}$, $\Delta_{fus}\boldsymbol{H}$, and $\Delta_{fus}\boldsymbol{S}$ at -3°C?

Question::

ice (1 atm, T) → liquid (1 atm, T)

Find: $\Delta_{fus}\boldsymbol{G}$ $\Delta_{fus}\boldsymbol{H}$ $\Delta_{fus}\boldsymbol{S}$ as a function of T

Consider the steps:

ice (1 atm, 273.2 K) → liquid (1 atm, 273.2 K) (a)

ice (1 atm, 273.2 K) → ice (1 atm, T) (b)

liq (1 atm, 273.2 K) → liq (1 atm, T) (c)

$\Delta_{fus}\boldsymbol{G}_T = \Delta\boldsymbol{G}_a - \Delta\boldsymbol{G}_b + \Delta\boldsymbol{G}_c$

$\boldsymbol{G} = \boldsymbol{H} - T\boldsymbol{S}$

$\Delta\boldsymbol{G}_a = 0$ ice and liq are at equilibrium

$\Delta\boldsymbol{G}_b = \Delta\boldsymbol{H}_b - (T\boldsymbol{S}_{ice,T} - 273.2\ \boldsymbol{S}_{ice,273})$

$\Delta\boldsymbol{G}_c = \Delta\boldsymbol{H}_c - (T\boldsymbol{S}_{liq,T} - 273.2\ \boldsymbol{S}_{liq,273})$

$\Delta\boldsymbol{H}_b = \int_{273}^{T} C_p^{ice}\mathrm{d}T = 0.48\times18\ (T-273)$

$\Delta\boldsymbol{H}_c = \int_{273}^{T} C_p^{LIQ}\mathrm{d}T = 1.0\times18\ (T-273)$

$$\boldsymbol{S}_{ice,T} = \boldsymbol{S}_{ice,273} + \int_{273}^{T}(C_p^{ice}/T)\mathrm{d}T$$
$$= \boldsymbol{S}_{ice,273} + 0.48\times18\ \ln(T/273)$$
$$\boldsymbol{S}_{liq,T} = \boldsymbol{S}_{liq,273} + \int_{273}^{T}(C_p^{liq}/T)\mathrm{d}T$$
$$= \boldsymbol{S}_{liq,273} + 1.0\times18\ \ln(T/273)$$

$$
\begin{aligned}
\Delta \boldsymbol{G}_b &= 0.48\times 18\ (T\text{-}273) \\
&\quad - T[\boldsymbol{S}_{ice,273} + 0.48\times 18\ \ln(T/273)] + 273\ \boldsymbol{S}_{ice,273} \\
&= 0.48\times 18\ (T\text{-}273) - (T\text{-}273)\boldsymbol{S}_{ice,273} \\
\Delta \boldsymbol{G}_c &= 1.0\times 18\ (T\text{-}273) \\
&\quad - T[\boldsymbol{S}_{liq,273} + 1.0\times 18\ \ln(T/273)] + 273\ \boldsymbol{S}_{liq,273} \\
&= 1.0\times 18\ (T\text{-}273) - (T\text{-}273)\boldsymbol{S}_{liq,273} \\
\Delta_{fus}\boldsymbol{G}_T &= \Delta \boldsymbol{G}_a - \Delta \boldsymbol{G}_b + \Delta \boldsymbol{G}_c \\
&= 0 - 0.48\times 18\ (T\text{-}273) + (T\text{-}273)\boldsymbol{S}_{ice,273} \\
&\qquad +1.0\times 18\ (T\text{-}273) - (T\text{-}273)\boldsymbol{S}_{liq,273} \\
&= (1.0 - 0.48)\times 18[(T\text{-}273) - T\ln(T/273)] \\
&\qquad + (T\text{-}273)(\boldsymbol{S}_{ice,273} - \boldsymbol{S}_{liq,273})
\end{aligned}
$$

$$
(\boldsymbol{S}_{ice,273} - \boldsymbol{S}_{liq,273}) = -\Delta_{fus}\boldsymbol{H}_{273}/273 = -79.7\times 18/273
$$

$$
\begin{aligned}
\therefore\ \Delta_{fus}\boldsymbol{G}_T &= 18\times \{(T\text{-}273)[(1.0 - 0.48) - 79.7/273] \\
&\qquad - (1.0 - 0.48)T\ln(T/273)\}
\end{aligned}
$$

$$
\Delta_{fus}\boldsymbol{G}_T = -1120.7 + 56.61T - 9.36T\ln T \text{ cal}
$$ Answer

$$
\begin{aligned}
\Delta_{fus}\boldsymbol{H}_T &= \Delta \boldsymbol{H}_a - \Delta \boldsymbol{H}_b + \Delta \boldsymbol{H}_c \\
&= 79.7\times 18 - 0.48\times 18\ (T\text{-}273) \\
&\qquad +1.0\times 18\ (T\text{-}273) \\
\Delta_{fus}\boldsymbol{H}_T &= \{(T\text{-}273)(1.0 - 0.48) + 79.7\}\times 18
\end{aligned}
$$

$$
\Delta_{fus}\boldsymbol{H}_T = -1120.7 + 9.36T \text{ cal}
$$ Answer

$\Delta_{fus}\boldsymbol{S}_T = \Delta\boldsymbol{S}_a - \Delta\boldsymbol{S}_b + \Delta\boldsymbol{S}_c$

$\mathrm{d}\boldsymbol{S} = \eth q_{REV}/T$

$\Delta\boldsymbol{S}_a = 79.7\times18/273$

$\mathrm{d}\boldsymbol{S} = (\partial\boldsymbol{S}/\partial T)_p \mathrm{d}T + (\partial\boldsymbol{S}/\partial p)_T \mathrm{d}p$

$\mathrm{d}\boldsymbol{S} = (C_p/T)\mathrm{d}T$ since $\mathrm{d}p = 0$

$\Delta\boldsymbol{S}_b = \int_{273}^{T} C_p^{ice}\mathrm{d}T/T = 0.48\times18 \ln(T/273)$

$\Delta\boldsymbol{S}_c = \int_{273}^{T} C_p^{LIQ}\mathrm{d}T/T = 1.0\times18 \ln(T/273)$

$\Delta_{fus}\boldsymbol{S}_T = \Delta\boldsymbol{S}_a - \Delta\boldsymbol{S}_b + \Delta\boldsymbol{S}_c$

$$\Delta_{fus}\boldsymbol{S}_T = 79.7\times18/273 - 0.48\times18 \ln(T/273) + 1.0\times18 \ln(T/273)$$

$\Delta_{fus}\boldsymbol{S}_T = \{(1.0-0.48)\ln(T/273) + 79.7/273\}\times18$

$\Delta_{fus}\boldsymbol{S}_T = -47.25 + 9.36\ln T$ cal Answer

Check that $\Delta_{fus}\boldsymbol{G}_T = \Delta_{fus}\boldsymbol{H} - T\Delta_{fus}\boldsymbol{S}$ holds. Start from

$\Delta_{fus}\boldsymbol{H}_T = -1120.7 + 9.36T$ cal

$\Delta_{fus}\boldsymbol{S}_T = -47.25 + 9.36\ln T$ cal

get

$\Delta_{fus}\boldsymbol{G}_T = -1120.7 + 56.61T - 9.36T\ln T$ cal

yes, agrees with $\Delta_{fus}\boldsymbol{G}_T$ obtained from sum of a,b,c.

$\Delta_{fus}\boldsymbol{G}_T/T = -1120.7/T + 56.61 - 9.36\ln T$

Now take the derivative

$[\partial(\Delta\boldsymbol{G}/T)/\partial T]_p = +1120.7/T^2 - 9.36/T$

This indeed agrees with

$-\Delta_{fus}\boldsymbol{H}/T^2 = +1120.7/T^2 - 9.36/T$

The problem suggested integrating the Gibbs Helmholtz eq. as a strategy:

$[\partial(\boldsymbol{G}_f/T)/\partial T]_p = -\boldsymbol{H}_f/T^2$ applied to liquid (1atm, T)

$\underline{[\partial(\boldsymbol{G}_i/T)/\partial T]_p = -\boldsymbol{H}_i/T^2}$ applied to ice (1atm, T)

$[\partial(\Delta \boldsymbol{G}/T)/\partial T]_p = -\Delta \boldsymbol{H}/T^2$

So if we had started out with

$[\partial(\Delta \boldsymbol{G}/T)/\partial T]_p = -\Delta \boldsymbol{H}/T^2$ and integrated,

$\int d(\Delta \boldsymbol{G}/T) = \int (-\Delta \boldsymbol{H}/T^2)dT$

This would mean that we need only to calculate

$\Delta_{fus}\boldsymbol{H}_T = -1120.7 + 9.36T$ cal

just as we did using steps a,b,c above.

we would have obtained

$\int d(\Delta \boldsymbol{G}/T) = \int (+1120.7/T^2 - 9.36/T)dT$

$(\Delta \boldsymbol{G}/T) = -1120.7/T - 9.36 \ln T + \text{constant}$

Let us now compare this with the $\Delta_{fus}\boldsymbol{G}_T/T$ that we had calculated using the steps a,b,c above:

$\Delta_{fus}\boldsymbol{G}_T/T = -1120.7/T + 56.61 - 9.36 \ln T$

It checks! and we find the constant of integration is +56.61 cal K^{-1}

---

at -3°C (270 K) event is spontaneous in reverse:

$\Delta_{fus}\boldsymbol{G}_T = -1120.7 + 56.61T - 9.36T\ln T = +15.67$ cal mol^{-1}

$\Delta_{fus}\boldsymbol{H}_T = -1120.7 + 9.36T = +1406.5$ cal mol^{-1}

$\Delta_{fus}\boldsymbol{S}_T = -47.25 + 9.36\ln T = +5.151$ cal $mol^{-1}K^{-1}$

4. Suppose 2.000 mol of neon (assumed to be an ideal gas) is confined in a strong, rigid container of volume 50.0 L at 304.66 K. The system is heated until 5000 J of heat has been added.

For this process, draw your initial and final pictures here

$n_{initial}$ =
$V_{initial}$ =
$T_{initial}$ =
$p_{initial}$ =

→

n_{final} =
V_{final} =
T_{final} =
p_{final} =

(a) The molar heat capacity of the gas does not change during the heating. ***What is the molar heat capacity*** of neon gas?

Using: ☐given in the problem ☐definition: ☐equation:

J mol^{-1}

(b) ***Calculate the original pressure*** inside the vessel (in atm)

Using: ☐given in the problem ☐definition: ☐equation:

$p_{initial}$ = atm

(c) ***Determine*** q ***for the system*** during the heating process

Using: ☐given in the problem ☐definition: ☐equation:

q = J

Problem **4.** continued on this page

(d) ***Determine*** w ***for the system*** during the heating process.

Using: ☐given in the problem ☐definition: ☐equation:

$w =$ J

(e) ***Compute the temperature of the gas*** after the heating. (Assume that the container itself has zero heat capacity)

Using: ☐given in the problem ☐definition: ☐equation:

T_{final} = K

(f) ***Compute the pressure*** (in atm) inside the vessel after the heating.

Using: ☐given in the problem ☐definition: ☐equation:

p_{final} = atm

(g) ***Compute change in the internal energy*** of the gas during the heating process.

Using: ☐given in the problem ☐definition: ☐equation:

$\Delta \boldsymbol{E} =$ J

Problem **4.** continued on this page.

(h) ***Compute the change in enthalpy*** of the gas during the heating process.

Using: ☐given in the problem ☐definition: ☐equation:

$\Delta H =$ J

(i) Correct answer to part (h) exceeds the amount of heat actually added. ***Explain why*** this is not a violation of the law of conservation of energy.

Using: ☐given in the problem ☐definition: ☐equation:

(j) ***Show*** the type of process when change of enthalpy equals the heat absorbed

Using: ☐given in the problem ☐definition: ☐equation:

(k) ***Calculate the change in entropy*** for this constant volume heating.

Using: ☐given in the problem ☐definition: ☐equation:

$\Delta S =$ J K^{-1}

Problem **4.** continued on this page

(l) Using the definition of ***G*** in terms of ***H*** and ***S***, ***what is the expression for the change in Gibbs free energy?***

Using: ☐given in the problem ☐definition: ☐equation:

(m) ***Calculate the change in Gibbs free energy*** for this constant volume heating. The standard entropy value for neon gas is $\boldsymbol{S}°$ at 298.15 K = 146.22 J K^{-1} mol^{-1}

Using: ☐given in the problem ☐definition: ☐equation:

$\Delta \boldsymbol{G}$ = J

(n) Suppose we had taken the neon gas from the original initial state to the same final state through a different path [for example, the 2-step sequence of : (i) isothermal compression to the final pressure, followed by (ii) constant pressure expansion to the final volume] instead, which of the following quantities for the overall 2-step process will be the same as calculated above for the constant volume heating? ***Circle as many as apply:***

ΔT	Δp	ΔV	Δn	q	w	$\Delta \boldsymbol{E}$	$\Delta \boldsymbol{H}$	$\Delta \boldsymbol{S}$	$\Delta \boldsymbol{G}$

4. Suppose 2.000 mol of neon (assumed to be an ideal gas) is confined in a strong, rigid container of volume 50.0 L at 304.66 K. The system is heated until 5000 J of heat has been added.

For this process, draw your initial and final pictures here

$n_{initial}$ = 2.000 mol
$V_{initial}$ = 50.0 L
$T_{initial}$ = 304.66 K
$p_{initial}$ = ? atm
C_V =

q =
+5000 J
→

n_{final} = 2.000
V_{final} = 50.0 L
T_{final} = ? K
p_{final} = ? atm

(a) The molar heat capacity of the gas does not change during the heating. ***What is the molar heat capacity*** of neon gas?

Using: ☐given in the problem ☒definition: ideal gas ☐equation: $\frac{1}{2} m\langle u^2\rangle = (3/2)k_B T$

for one mole of a monatomic ideal gas, $E = E_0 + \frac{1}{2} m\langle u^2\rangle N_{Avog} = E_0 + (3/2)RT$

so that $C_V = (3/2)R = (3/2)(\ 8.31451\text{J K}^{-1}\text{ mol}^{-1}\ ) =$

12.472 J mol^{-1}

(b) ***Calculate the original pressure*** inside the vessel (in atm)

Using: ☐given in the problem ☐definition: ☒equation: $pV=nRT$

$p(50.0\text{ L}) = (2.0\text{ mol})(\ 0.0820578\text{ L atm K}^{-1}\text{ mol}^{-1}\ )(304.66\text{ K})$

p = 1.00 atm

$p_{initial}$ = 1.00 atm

(c) ***Determine q for the system*** during the heating process

Using: ☒given in the problem ☐definition: ☐equation:

q = +5000 J

Problem **4.** continued on this page

(d) ***Determine*** w ***for the system*** during the heating process.

Using: ☐given in the problem ☒definition: $\mathrm{d}w = -p_{oppposing}\mathrm{d}V$ ☐equation:

$\mathrm{d}V = 0$ (rigid container no change in V) therefore $\mathrm{d}w = 0$

$w =$ 0 J

(e) ***Compute the temperature of the gas*** after the heating. (Assume that the container itself has zero heat capacity)

Using: ☐given in the problem ☒definition: $\mathrm{d}q = C\mathrm{d}T$ ☐equation:

$C = (3/2)R$ does not change (given)

so $q = C\Delta T = C(T_{final} - T_{initial})$

$5000 \text{ J} = 2.0 \text{ mol } (3/2)(8.31451 \text{J K}^{-1} \text{ mol}^{-1})(T_{final} - 304.66 \text{ K})$

Solve for T_{final}

$T_{final} =$ 505.11 K

(f) ***Compute the pressure*** (in atm) inside the vessel after the heating.

Using: ☐given in the problem ☐definition: ☒equation: $pV=nRT$

$p_{final}(50.0 \text{ L}) = (2.0 \text{ mol})(0.0820578 \text{ L atm K}^{-1} \text{ mol}^{-1})(505.11 \text{ K})$

Solve for $p_{final} = 2.0\times0.0820578\times505.11 / 50.0$

$p_{final} =$ 1.658 atm

(g) ***Compute change in the internal energy*** of the gas during the heating process.

Using: ☐given in the problem ☐definition: ☒equation: $\Delta E = q + w$

First law provides $\Delta E = q + w = 5000 + 0$

$\Delta E =$ 5000 J

Problem **4.** continued on this page.

(h) ***Compute the change in enthalpy*** of the gas during the heating process.

Using: ☐given in the problem ☒definition: $H \equiv E + pV$ ☐equation:

$H \equiv E + pV$ means that the change is

$\Delta \boldsymbol{H} = \Delta \boldsymbol{E} + p_{final}\, V_{final} - p_{initial}\, V_{initial}$

$= 5000\ \text{J} + (1.658\ \text{atm} - 1.000\ \text{atm})50.0\ \text{L}$

$\times(8.31451\text{J K}^{-1}\ \text{mol}^{-1})/(\ 0.0820578\ \text{L atm K}^{-1}\ \text{mol}^{-1}) = 5000+3333.6$

$\Delta \boldsymbol{H} =$ 8333.6 J

(i) Correct answer to part (h) exceeds the amount of heat actually added. ***Explain why*** this is not a violation of the law of conservation of energy.

Using: ☐given in the problem ☒definition: First law: ***E*** is conserved ☐equation:

The law of conservation of energy applies to energy, not enthalpy.

(j) ***Show*** the type of process when change of enthalpy equals the heat absorbed

Using: ☐given in the problem ☒definition: $\boldsymbol{H} = \boldsymbol{E} + pV$, $\Delta \boldsymbol{E} = q + w$ ☐equation:

Constant pressure process: $w_p = -\, p_{opposing}(V_{final} - V_{initial})$

and $\Delta \boldsymbol{H} = \Delta \boldsymbol{E} + p(V_{final} - V_{initial})$

Combining this with First Law: $\Delta \boldsymbol{E} = q_p + w_p$

leads to $\Delta \boldsymbol{H} = q_p$

(k) ***Calculate the change in entropy*** for this constant volume heating.

Using: ☐given in the problem ☒definition: $d\boldsymbol{S} = dq_{rev}/T$ ☐equation:

Carry out the heating at constant volume in a reversible manner,

$dq = C_V\, dT = dq_{rev}$, so that $d\boldsymbol{S} = C_V\, dT/T$, which when summed up gives

$\Delta \boldsymbol{S} = C_V \ln(T_{final}/T_{initial}) = 2.0\ \text{mol}\times 3/2 \times(\ 8.31451\text{J K}^{-1}\text{mol}^{-1})\ln(505.11/304.66)$

$\Delta \boldsymbol{S} =$ 12.61 J K^{-1}

Problem **4.** continued on this page

(l) Using the definition of ***G*** in terms of ***H*** and ***S***, ***what is the expression for the change in Gibbs free energy?***

Using: ☐given in the problem ☒definition: $G \equiv H - TS$ ☐equation:

$\Delta G = \Delta H - (T_{final} S_{final} - T_{initial} S_{initial})$

(m) ***Calculate the change in Gibbs free energy*** for this constant volume heating. The standard entropy value for neon gas $S°$ at 298.15 K = 146.22 J K^{-1} mol^{-1}.

Using: ☒given in the problem $S°_{298.15\ K} = 146.22$ J K^{-1} mol^{-1} ☒definition: $S_{0K} = 0$

☒equation: $\Delta S_V = C_V \ln(T_{final}/T_{initial})$ derived in part (k)

From $q_{rev}/T = -w_{rev}/T$ when $\Delta E = 0$, we find $\Delta S_T = nR\ln(V_{final}/V_{initial})$

Third law plus equation derived in part (k) and above gives

$S_{final} = S°_{298\ K} + C_V \ln(T_{final}/298.15) + \Delta S\ (1\ \text{atm} \rightarrow 1.658\ \text{atm})$

$= 146.22 + 2.0(3/2)(8.31451)\ln(505.11/298.15) + 2.0(8.31451)\ln(1/1.658)$

$= 146.22 + 13.15 - 8.41 = 150.96\ \text{J K}^{-1}$

$S_{initial} = S°_{298\ K} + C_V \ln(T_{initial}/298.15)$ at 1 atm

$= 146.22 + 2.0(3/2)(8.31451)\ln(304.66/298.15)$

$= 146.22 + 0.539 = 146.76\ \text{J K}^{-1}$

$\Delta G = \Delta H - (T_{final} S_{final} - T_{initial} S_{initial})$

$= 8333.6\ \text{J} - (505.11 \times 150.96 - 304.66 \times 146.76)\ \text{J}$

$= 8333.6 - 31\,539.5 = -23\,205.9\ \text{J}$

$\Delta G = -23\,205.9$ J

(n) Suppose we had taken the neon gas from the original initial state to the same final state through a different path [for example, the 2-step sequence of : (i) isothermal compression to the final pressure, followed by (ii) constant pressure expansion to the final volume] instead, which of the following quantities for the overall 2-step process will be the same as calculated above for the constant volume heating? ***Circle as many as apply:***

[✓ (ΔT)]	[✓ (Δp)]	[✓ (ΔV)]	[✓ (Δn)]	q	w	[✓ (ΔE)]	[✓ (ΔH)]	[✓ (ΔS)]	[✓ (ΔG)]

Example:

Two moles of a gas whose equation of state is $pV = RT + ap$

where a has the following values

a, L mol^{-1}	T, K
0.020	300
0.025	400
0.030	500

undergoes isothermal compression at 300 K from 1 atm to 11 atm.

Questions:

Calculate $\Delta \boldsymbol{G}$, $\Delta \boldsymbol{S}$, $\Delta \boldsymbol{H}$ for the gas.

EXAMPLE:

3. Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections $\mathcal{A}$ and $\mathcal{B}$. All changes in $\mathcal{B}$ are isothermal, that is a thermostat surrounds $\mathcal{B}$ to keep its temperature constant. There is 2.00 mol of the gas in each section. Initially $T_{\mathcal{A}} = T_{\mathcal{B}} = 300$ K, $V_{\mathcal{A}} = V_{\mathcal{B}} = 2.00$ L. Heat is added to section $\mathcal{A}$ and the piston moves to the right <u>reversibly</u> until the final volume of section $\mathcal{B}$ is 1.00 L .

Calculate the work done by the gas in section $\mathcal{A}$. Calculate for the gas in each section: $\Delta \boldsymbol{U}$, q, $\Delta \boldsymbol{S}$, $\Delta \boldsymbol{A}$, $\Delta \boldsymbol{H}$, $\Delta \boldsymbol{G}$.

Calculate $\Delta \boldsymbol{S}$ of the total system and its surroundings.

Assume $C_V = 20\ \text{J K}^{-1}\ \text{mol}^{-1}$.

Ideal: $C_p = 28.3144\ \text{J K}^{-1}\ \text{mol}^{-1}$.

Example:

Two moles of a gas whose equation of state is $pV = RT + ap$
where a has the following values

a, L mol^{-1}	T, K
0.020	300
0.025	400
0.030	500

undergoes isothermal compression at 300 K from 1 atm to 11 atm.

Questions:

Calculate $\Delta \boldsymbol{G}$, $\Delta \boldsymbol{S}$, $\Delta \boldsymbol{H}$ for the gas.

$pV = RT + a(T)p$

V_i
300 K
1 atm
2 mol

$\xrightarrow[dT = 0]{}$

V_f
300 K
11 atm
2 mol

From $\boldsymbol{G} = \boldsymbol{H} - \boldsymbol{TS}$ and $\boldsymbol{H} = \boldsymbol{U} + pV$

$$d\boldsymbol{G} = d\boldsymbol{H} - Td\boldsymbol{S} - \boldsymbol{S}dT$$

$$= d\boldsymbol{U} + pdV + Vdp - Td\boldsymbol{S} - \boldsymbol{S}dT$$

apply $d\boldsymbol{S} = d\boldsymbol{q}_{\mathrm{REV}}/T$

and $d\boldsymbol{U} = d\boldsymbol{q}_{\mathrm{REV}} + d\boldsymbol{W}_{\mathrm{REV}} = d\boldsymbol{q}_{\mathrm{REV}} - pdV$

to derive $d\boldsymbol{G} = -\boldsymbol{S}dT + Vdp$

For this problem, $dT = 0$ leads to

$$\Delta \boldsymbol{G} = n\int_1^{11}\left(\frac{RT}{p} + a\right)dp$$

$$\Delta \boldsymbol{G} = 2\{0.08205 \times 300 \times \ln(11/1) + 0.020 \times (11-1)\} \times (1.987/0.08205)\ \mathrm{cal}$$

Consider the state function $\boldsymbol{S}(T,p)$:

$\mathrm{d}\boldsymbol{S} = (\partial \boldsymbol{S}/\partial T)_p \mathrm{d}T + (\partial \boldsymbol{S}/\partial p)_T \mathrm{d}p$

First derive $(\partial \boldsymbol{S}/\partial p)_T$:

$\mathrm{d}\boldsymbol{G} = - \boldsymbol{S}\mathrm{d}T + V\mathrm{d}p$ derived above leads to equal cross-derivatives

$-(\partial \boldsymbol{S}/\partial p)_T = (\partial V/\partial T)_p$

From the eqn of state:

$pV = \mathrm{R}T + \mathrm{a}(T)p$ we rearrange to get

$V = (\mathrm{R}T/p) + \mathrm{a}(T)$

$(\partial V/\partial T)_p = (\mathrm{R}/p) + \mathrm{da}/\mathrm{d}T$

$= (\mathrm{R}/p) + 0.5\times10^{-4}$ given table

To get $\Delta \boldsymbol{S}$ when $\mathrm{d}T = 0$,

$$\Delta \boldsymbol{S} = -n\int_1^{11}\left(\frac{R}{p} + 0.5\times10^{-4}\right)dp$$

$$\Delta \boldsymbol{S} = -2\{0.08205\times\ln(11/1) + 0.5\times10^{-4}\times(11-1)\}\times(1.987/0.08205)\ \mathrm{cal\ K^{-1}}$$

Consider the state function $\boldsymbol{H}(T,p)$:

$d\boldsymbol{H} = (\partial\boldsymbol{H}/\partial T)_p dT + (\partial\boldsymbol{H}/\partial p)_T dp$

First derive $(\partial\boldsymbol{H}/\partial p)_T$:

using cross-derivatives (see lectures)

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

From the eqn of state:

$pV = RT + a(T)p$ we rearrange to get

$V = (RT/p) + a(T)$

$$(\partial V/\partial T)_p = (R/p) + da/dT$$
$$= (R/p) + 0.5\times10^{-4}$$

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

$= -(RT/p) - 0.5\times10^{-4}T + (RT/p) + a$

$= -0.5\times10^{-4}T + a = 0.035$ at $T=300$ K

To get $\Delta\boldsymbol{H}$ when $dT = 0$,

$$\Delta\boldsymbol{H} = -n\int_1^{11} 0.035\,dp$$

$$\Delta\boldsymbol{H} = -2\times0.035\times(11-1)\times1.987/\ 0.08205 \text{ cal}$$

EXAMPLE:

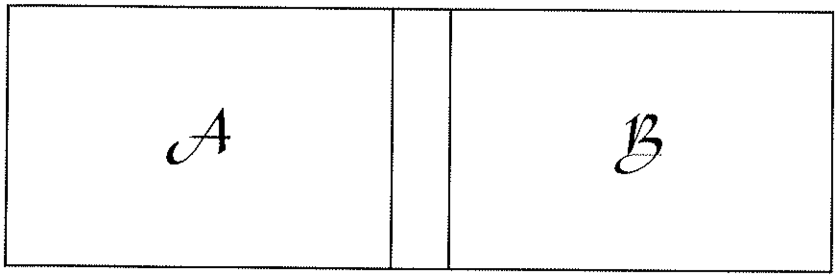
3. Consider a perfect gas contained in a cylinder and separated by a frictionless adiabatic piston into two sections $\mathcal{A}$ and $\mathcal{B}$. All changes in $\mathcal{B}$ are isothermal, that is a thermostat surrounds $\mathcal{B}$ to keep its temperature constant. There is 2.00 mol of the gas in each section. Initially $T_{\mathcal{A}} = T_{\mathcal{B}} = 300$ K, $V_{\mathcal{A}} = V_{\mathcal{B}} = 2.00$ L. Heat is added to section $\mathcal{A}$ and the piston moves to the right <u>reversibly</u> until the final volume of section $\mathcal{B}$ is 1.00 L .

Calculate the work done by the gas in section $\mathcal{A}$. Calculate for the gas in each section: $\Delta \boldsymbol{U}$, q, $\Delta \boldsymbol{S}$, $\Delta \boldsymbol{A}$, $\Delta \boldsymbol{H}$, $\Delta \boldsymbol{G}$.

Calculate $\Delta \boldsymbol{S}$ of the total system and its surroundings.

Assume $C_V = 20 \text{ J K}^{-1} \text{ mol}^{-1}$.

Ideal: $C_p = 28.3144 \text{ J K}^{-1} \text{ mol}^{-1}$.



$n = 2$ moles	$n = 2$ moles
initial	initial
$T = 300$ K	$T = 300$ K
$V = 2$ L	$V = 2$ L
p =?=24.6 atm	p = ? = 24.6 atm
final	final
T = ? K	$T = 300$ K (isothermal)
V = ? = 3 L	$V = 1$ L (given)
p =same as $\mathcal{B}$	p = ? = 49.2 atm
$\therefore$ find T=900K	

Work done on the gas in section $\mathcal{B}$

$W_{\mathcal{B}} = -\int p_{op}\,\mathrm{d}V$ (reversibly) $= -\int p_{gas}\,\mathrm{d}V$

$= -\int nRT\mathrm{d}V/V$ ($p = nRT/V$, ideal gas)

$= -2 \times 8.3144 \times 300 \times \ln(1/2) = +3.46$ kJ

$W_{\mathcal{A}} = -3.46$ kJ

$\Delta \boldsymbol{U}$, q, $\Delta \boldsymbol{S}$, $\Delta \boldsymbol{A}$, $\Delta \boldsymbol{H}$, and $\Delta \boldsymbol{G}$:

	$\mathcal{A}$	$\mathcal{B}$
W_{rev}	- 3.46 kJ	+ 3.46 kJ
$\Delta \boldsymbol{U}$	ideal $\boldsymbol{U} = \boldsymbol{U}(T)$ $\Delta \boldsymbol{U} = \int C_V \, \mathrm{d}T$ $=2\times20\times(900-300)$ $= 24$ kJ	ideal $\boldsymbol{U} = \boldsymbol{U}(T)$ $\mathrm{d}T = 0$ $\Delta \boldsymbol{U} = 0$
q	$\Delta \boldsymbol{U} = q + W$ $q = 27.46$ kJ	$\Delta \boldsymbol{U} = q + W$ $q = -3.46$ kJ
$\Delta \boldsymbol{S}$	$\mathrm{d}\boldsymbol{S} = (1/T)C_p \, \mathrm{d}T$ $- (\partial V/\partial T)_p \, \mathrm{d}p$ $\Delta \boldsymbol{S} = n\int C_p \, \mathrm{d}T/T$ $- n\int R\mathrm{d}p/p$ $=2\times28.3144\times$ $\ln(900/300)$ $- 2\times8.3144\times$ $\ln(49.2/24.6)$ $= +50.7$ J K^{-1}	$\mathrm{d}\boldsymbol{S} = (1/T)C_p \, \mathrm{d}T$ $- (\partial V/\partial T)_p \, \mathrm{d}p$ $\mathrm{d}T=0$ $\Delta \boldsymbol{S} = - n\int R\mathrm{d}p/p$ $= - 2\times8.3144\times$ $\ln(49.2/24.6)$ $= - 11.53$ J K^{-1}
$\Delta \boldsymbol{A}$	$\Delta \boldsymbol{A}$ = ?, $dT\neq0$ $\neq$ - 3.46 kJ	$\Delta \boldsymbol{A}_T = W_{rev} =$ $W_{max} = + 3.46$ kJ

$\Delta \boldsymbol{H}$	ideal $\boldsymbol{H} = \boldsymbol{H}(T)$ $\Delta \boldsymbol{H} = n \int C_p \, \mathrm{d}T$ $= 2 \times 28.3144 \times$ $(900-300)$ $= 33.98$ kJ	ideal $\boldsymbol{H} = \boldsymbol{H}(T)$ $\mathrm{d}T = 0$ $\Delta \boldsymbol{H} = 0$
$\Delta \boldsymbol{G}$	$\Delta \boldsymbol{G} = \Delta \boldsymbol{H} - \Delta(T\boldsymbol{S})$ need to calculate $\boldsymbol{S}$ at initial and final states	$\Delta \boldsymbol{G}_T = \Delta \boldsymbol{H} - T\Delta \boldsymbol{S}$ $= -T\Delta \boldsymbol{S}$ $= 11.53 \times 300$ J $= 3.46$ kJ

$$\Delta \boldsymbol{S}_{\text{system}} = \Delta \boldsymbol{S}_{\mathcal{A}} + \Delta \boldsymbol{S}_{\mathcal{B}} = +50.7 - 11.53$$
$$= +39.2 \text{ J K}^{-1}$$

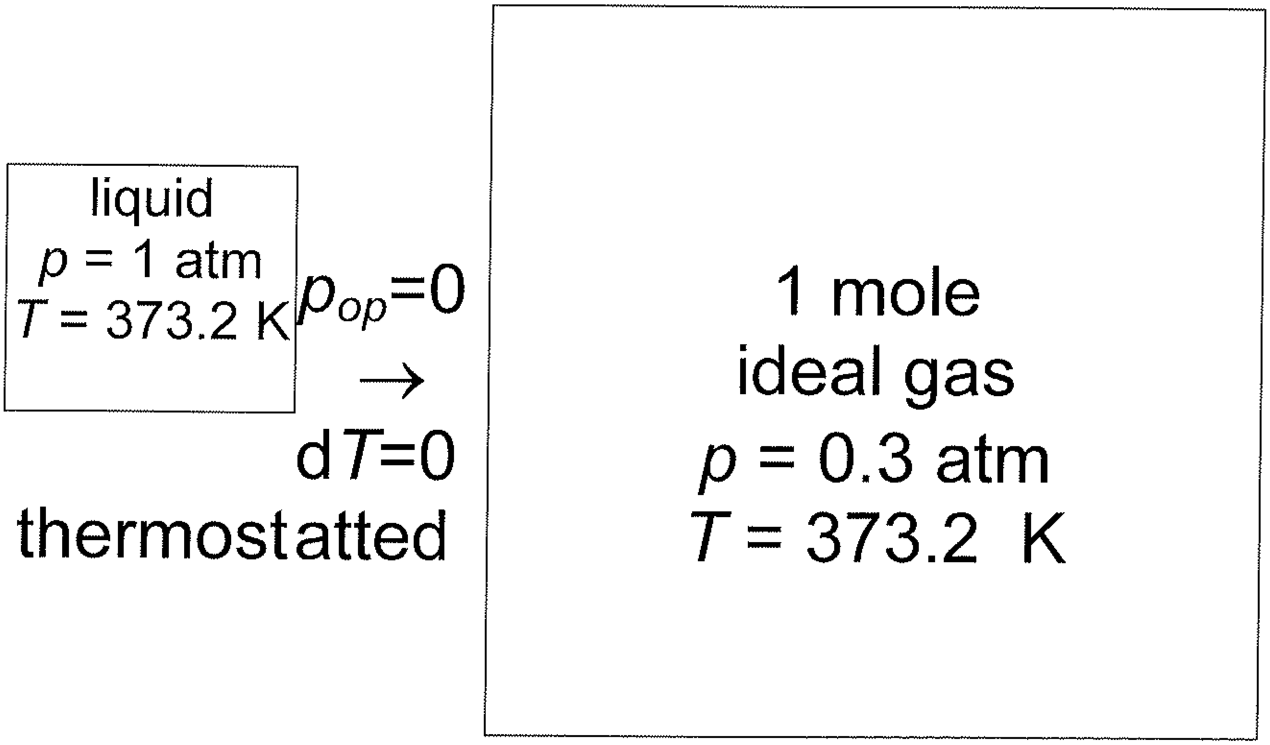
$$\Delta \boldsymbol{S}_{\text{surrounding}} = -39.2 \text{ J K}^{-1}$$

since process was carried out reversibly

EXAMPLE: 3 (b) One mole of liquid water (density = 1 g/mL) is allowed to expand into an evacuated flask of volume such that the final pressure is 0.3 atm. The bulb containing the liquid and the flask are thermostated so that a constant temperature of 100 °C is maintained. It is found that 11,000 cal of heat are absorbed when this process occurs. Calculate the values for ΔU, ΔH, ΔS, and ΔG. Assume vapor is ideal.

EXAMPLE: 3 (b) One mole of liquid water (density = 1 g/mL) is allowed to expand into an evacuated flask of volume such that the final pressure is 0.3 atm. The bulb containing the liquid and the flask are thermostated so that a constant temperature of 100 °C is maintained. It is found that 11,000 cal of heat are absorbed when this process occurs. Calculate the values for $\Delta \boldsymbol{U}$, $\Delta \boldsymbol{H}$, $\Delta \boldsymbol{S}$, and $\Delta \boldsymbol{G}$. Assume vapor is ideal.

Draw a Picture



liquid
p = 1 atm
T = 373.2 K

p_{op}=0
→
dT=0
thermostatted

1 mole
ideal gas
p = 0.3 atm
T = 373.2 K

$\Delta \boldsymbol{U}$ = ?

Given: $p_{op} = 0$ $q = 11{,}000$ cal

$\delta W = p_{op}\mathrm{d}V = 0$

$\therefore \Delta \boldsymbol{U} = q + W = 11{,}000$ cal

$\Delta \boldsymbol{H}$ = ?

$\boldsymbol{H} \equiv \boldsymbol{U} + pV$ $V_{liq} = 18\times10^{-3}$ L

$\Delta \boldsymbol{H} = \Delta \boldsymbol{U} + \Delta(pV)$ $(pV)_{\mathrm{gas}} = RT$

$= 11{,}000 + [(pV)_{\mathrm{gas}} - (pV)_{\mathrm{liq}}]$

$= 11{,}000 +$

$[1.987\times373.2 - 18\times10^{-3}\times1.987/0.082057]$

$= 11{,}740$ cal

$\Delta \boldsymbol{S} = ?$

ΔS is not 11000/373.2 ! <u>not reversible</u>

construct ***reversible*** *steps leading to*

liq, 1 atm, 373.2 K →gas, 0.3 atm, 373.2

(a) liq, 1 atm, 373.2 → gas, 1 atm, 373.2

(b) gas, 1 atm, 373.2 K → gas, 0.3 atm, 373.2 K

$$\Delta \boldsymbol{S} = \Delta \boldsymbol{S}_a + \Delta \boldsymbol{S}_b \qquad \Delta \boldsymbol{H} = \Delta \boldsymbol{H}_a + \Delta \boldsymbol{H}_b$$

$$\text{use} \quad \begin{cases} \mathrm{d}\boldsymbol{S} \equiv \eth q_{rev}/T \\ \mathrm{d}\boldsymbol{S} = (\partial \boldsymbol{S}/\partial T)_p\, \mathrm{d}T + (\partial \boldsymbol{S}/\partial p)_T\, \mathrm{d}p \end{cases}$$

$$\mathrm{d}\boldsymbol{S} = (C_p/T)\mathrm{d}T \quad - (\partial V/\partial T)_p\, \mathrm{d}p$$

(as derived in part a of this problem)

$$\Delta \boldsymbol{H}_b = \int(\partial \boldsymbol{H}/\partial T)_p\, \underline{\mathrm{d}T} + \int\underline{(\partial \boldsymbol{H}/\partial p)_T}\, \mathrm{d}p = 0 + 0$$

$$\Delta \boldsymbol{H} = 11{,}740 = \Delta \boldsymbol{H}_a + \Delta \boldsymbol{H}_b = \Delta \boldsymbol{H}_a + 0$$

$$\Delta \boldsymbol{S}_a = q_{rev}/T = \Delta \boldsymbol{H}_a/T = 11{,}740/373.2$$

$$\Delta \boldsymbol{S}_b = \int -(\partial V/\partial T)_p\, \mathrm{d}p = -\int_1^{0.3}(R/p)dp$$

$$= -1.987 \ln(0.3/1)$$

$$\Delta \boldsymbol{S} = 11740/373.2 + 1.987 \ln(1/0.3)$$

$$= 33.85 \text{ cal K}^{-1}$$

$\Delta \boldsymbol{S}_{surr}$ **= ?**

$\Delta \boldsymbol{S}_{surr} = -11000/373.2 = -29.49$

$\Delta \boldsymbol{S}_{universe} = 33.85 - 29.49 =$ positive

spontaneous change!

$\Delta \boldsymbol{G}$ **= ?**

$$\Delta \boldsymbol{G}_T = \Delta \boldsymbol{H} - T\Delta \boldsymbol{S} = 11740 - 373.2\times 33.85$$

$$= 11740 - 12632.8 \quad = -\ 892.8 \text{ cal}$$

or else

$\Delta \boldsymbol{G} = \Delta \boldsymbol{G}_a + \Delta \boldsymbol{G}_b$

$\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\underline{\mathrm{d}T}$

(as derived in part a of this problem)

$\mathrm{d}T = 0$ for all steps

$$\Delta \boldsymbol{G}_b = \int V\mathrm{d}p = \int_1^{0.3} (RT/p)dp$$

$$= 1.987\times 373.2\times \ln (0.3/1) = -\ 892.8 \text{ cal}$$

$\Delta \boldsymbol{G}_a = 0$ gas and liq are at equilibrium

$\Delta \boldsymbol{G} = -\ 892.8$ cal

$\Delta \boldsymbol{A}$ **= ?**

$$\Delta \boldsymbol{A} = \Delta \boldsymbol{U} - T\Delta \boldsymbol{S} = 11000 - 12633 = -1633$$

or $\mathrm{d}\boldsymbol{A} = -p\mathrm{d}V - \boldsymbol{S}\underline{\mathrm{d}T} \quad \therefore \quad -\int p\mathrm{d}V = -1633$ cal

Maximum work = $W_{max} = W_a + W_b$

$W_a = -1\int \mathrm{d}V = -1\{RT/1 - 18\times10^{-3}\ \mathrm{L}\},\quad p_{op}=1$

$= -740$ cal

$W_b = -\int p_{op}\mathrm{d}V = -\int (RT/V)\mathrm{d}V = -RT\ln(V_f/V_i)$

$(V_f/V_i) = [RT/0.3] \div [RT/1] = 1/0.3$

$W_b = -1.987\times373.2\times\ln(1/0.3) = -892.8$ cal

$W_{max} = -740 - 892.8 = -1633$ cal $= -\int p\mathrm{d}V$

$W_{max} = \Delta \boldsymbol{A}_T = -1633$ cal

An example of multiple approaches to a given problem:

Exam Problem 3(b) One mole of liquid water (density = 1 g/mL) is allowed to expand into an evacuated flask of volume such that the final pressure is 0.3 atm. The bulb containing the liquid and the flask are thermostated so that a constant temperature of 100 °C is maintained. It is found that 11,000 cal of heat are absorbed when this process occurs. Calculate the values for $\Delta \boldsymbol{U}$, $\Delta \boldsymbol{H}$, $\Delta \boldsymbol{S}$, and $\Delta \boldsymbol{G}$. Assume vapor is ideal.

$\mathrm{d}T = 0$ for this system

	cal mol^{-1}	from definition of the function	from relations derived from First and Second Law
$\Delta \boldsymbol{U}$	11,000	$q_{IRREV}+W_{IRREV}$ = 11,000 + 0 $q_{REV}+W_{REV}$ = 12,633 + - 1633 = 11,000	$T\Delta \boldsymbol{S} - \int p\mathrm{d}V$ = 12,633 - 1633 = 11,000
$\Delta(pV)$	740	$p_fV_f - p_iV_i$ = RT - 1atm×0.018 L mol^{-1} = 741.2 - 0.436 ≈ 740	
$\Delta \boldsymbol{H}$	11,740	$\Delta \boldsymbol{U} + \Delta(pV)$ = 11,000 + 740 = 11,740	$T\Delta \boldsymbol{S} + \int V\mathrm{d}p$ = 12,633 - 843 = 11,740
$T\Delta \boldsymbol{S}$	12,633	q_{REV} = 12,633	
$\Delta \boldsymbol{G}$	-893	$\Delta \boldsymbol{H} - T\Delta \boldsymbol{S}$ = 11,740 - (12,633) = -893	$-\int \boldsymbol{S}\underline{\mathrm{d}T} + \int V\mathrm{d}p$ = 0 + (-893) = -893
$\int V\mathrm{d}p$	-893		
$\int p\mathrm{d}V$	1633	$-W_{REV}$	
$\Delta \boldsymbol{A}$		$\Delta \boldsymbol{U} - T\Delta \boldsymbol{S}$ = 11,000 - (12,633) = -1633	$-\int p\mathrm{d}V - \int \boldsymbol{S}\underline{\mathrm{d}T}$ = -1633 + 0 = -1633
$\Delta \boldsymbol{S}_{sys}$	33.87 cal mol^{-1} K^{-1}	q_{REV}/T = 12,633/373 = 33.87 = $\Delta_{vap}\boldsymbol{H}/T - \int R\mathrm{d}p/p$ = 11740/373 - $R\ln(0.3/1)$ = 31.47+2.39 = 33.86	
$\Delta \boldsymbol{S}_{surr}$	-29.49	$(q_{REV})_{surr}/T$ = -11,000/373 = -29.49	

	cal mol^{-1}	from considering a function of two variables
$\Delta \boldsymbol{U}$	11,000	$\Delta_{vap}\boldsymbol{U}$ = 11,000 for phase change + from $\mathrm{d}\boldsymbol{U} = (\partial \boldsymbol{U}/\partial T)_V\,\underline{\mathrm{d}T} + \underline{(\partial \boldsymbol{U}/\partial V)_T}\,\mathrm{d}V$ $= \quad 0 \quad + 0$ total = 11,000
$\Delta(pV)$	740	
$\Delta \boldsymbol{H}$	11,740	$\Delta_{vap}\boldsymbol{H}$ = 11,740 for phase change + from $\mathrm{d}\boldsymbol{H} = (\partial \boldsymbol{H}/\partial T)_p\underline{\mathrm{d}T} + \underline{(\partial \boldsymbol{H}/\partial p)_T}\,\mathrm{d}p$ $= \quad 0 \quad + 0$
$T\Delta \boldsymbol{S}$	12,633	
$\Delta \boldsymbol{G}$	-893	$\Delta_{vap}\boldsymbol{G}$ = 0 for phase change + from $\mathrm{d}\boldsymbol{G} = (\partial \boldsymbol{G}/\partial T)_p\,\mathrm{d}T + (\partial \boldsymbol{G}/\partial p)_T\,\mathrm{d}p$ $= \quad -\boldsymbol{S}\underline{\mathrm{d}T} + V\mathrm{d}p$ $= \quad 0 + (-893) = -893$
$\int V\mathrm{d}p$	-893	
$\int p\mathrm{d}V$	1633	$-W_{REV}$ {*Note that* $\Delta \boldsymbol{A}$ *gives the maximum work done by the system*}
$\Delta \boldsymbol{A}$		$\mathrm{d}\boldsymbol{A} = (\partial \boldsymbol{A}/\partial T)_V\,\mathrm{d}T + (\partial \boldsymbol{A}/\partial V)_T\,\mathrm{d}V$ $= \quad -\int \boldsymbol{S}\underline{\mathrm{d}T} - \int p\mathrm{d}V$ $= \quad 0 - 1633 = -1633$
$\Delta \boldsymbol{S}_{sys}$	33.87 cal mol^{-1} K^{-1}	$\Delta_{vap}\boldsymbol{H}/T$= 11740/373 + for the next *rev* step: $\mathrm{d}\boldsymbol{S} = (\partial \boldsymbol{S}/\partial T)_p\,\underline{\mathrm{d}T} + (\partial \boldsymbol{S}/\partial p)_T\,\mathrm{d}p$ $= \quad 0 - (\partial \boldsymbol{V}/\partial T)_p\mathrm{d}p$ $= \quad 0 - R\ln(0.3/1)$ $= \quad +2.39$ total = 31.47+2.39 = 33.86
$\Delta \boldsymbol{S}_{surr}$	-29.49	