

Meerkeuzevragen

1. According to the second law, $\left(\frac{\partial \bar{v}}{\partial p}\right)_T$ is always:
 - a) ≥ 0 (positive) and for incompressible liquids $\rightarrow 0$
 - b) ≥ 0 (positive) and for incompressible liquids $\rightarrow +\infty$
 - c) ≤ 0 (negative) and for incompressible liquids $\rightarrow 0$
 - d) ≤ 0 (negative) and for incompressible liquids $\rightarrow -\infty$
2.
 - a) The enthalpy has a molecular interpretation as the mean kinetic and potential energy of all considered molecules
 - b) The enthalpy is a pragmatic quantity, which is useful for closed isobaric systems and for open processes
 - c) The enthalpy is a measure for the number of molecular configurations
 - d) The enthalpy is a conserved property ; it can not be created or destroyed, but only converted
3. The heat capacity at constant pressure is
 - a) $c_p = \left(\frac{dh}{dT}\right)_p = T \left(\frac{ds}{dT}\right)_p$
 - b) $c_p = \left(\frac{du}{dT}\right)_p = T \left(\frac{ds}{dT}\right)_p$
 - c) $c_p = \left(\frac{dh}{dT}\right)_p = T \left(\frac{dq}{dT}\right)_p$
 - d) $c_p = \left(\frac{dh}{dT}\right)_p = T \left(\frac{ds}{dT}\right)_v$
4. The fundamental equation for the internal energy U is given as
 - a) $U(V, S, \mu_i)$
 - b) $U(V, T, \mu_i)$
 - c) $U(V, S, n_i)$
 - d) $U(V, T, n_i)$
5. The Clausius equation in the form $\left(\frac{dp}{dT}\right)_{I \rightarrow II} = \frac{\Delta^{I \rightarrow II} \bar{h}}{T(\bar{v}^{II} - \bar{v}^I)}$ (where I and II are indices for a phase I and phase II, respectively) can be applied to
 - a) the vapor pressure curve, only
 - b) the vapor pressure and the sublimation pressure curve
 - c) the vapor pressure and the melting pressure curve
 - d) the vapor pressure, the sublimation pressure curve, and the melting pressure curve

6. The Clausius-Clapeyron equation in the form $\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta^{l \rightarrow H} \bar{h}}{\bar{R}} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

(caution: in an earlier version of this document the natural logarithm in this equation was missing) can be derived from the Clausius equation (question 3) by assuming:

- a) $\bar{v}^{vapor} \gg \bar{v}^{liquid}$, ideal gas the vapor, isochoric process
- b) $\bar{v}^{vapor} \gg \bar{v}^{liquid}$, ideal gas the vapor, $\delta Q = 0$ (adiabaat)
- c) $\bar{v}^{vapor} \gg \bar{v}^{liquid}$, ideal gas for vapor, chemical potential is constant
- d) $\bar{v}^{vapor} \gg \bar{v}^{liquid}$, ideal gas for vapor, enthalpy of vaporization is constant

7. The Van der Waals equation of state (with positive parameters a and b) has the form

- a) $p = \frac{\bar{R}T}{\bar{v} + b} - \frac{a}{\bar{v}^2}$
- b) $p = \frac{\bar{R}T}{\bar{v} + b} + \frac{a}{\bar{v}^2}$
- c) $p = \frac{\bar{R}T}{\bar{v} - b} - \frac{a}{\bar{v}^2}$
- d) $p = \frac{\bar{R}T}{\bar{v} - b} + \frac{a}{\bar{v}^2}$

8. The chemical potential of a pure component:
- is equal to the Gibbs energy. It can be calculated knowing the vapor pressure curve of a substance and the ideal gas heat capacity.
 - is equal to the Gibbs energy. It can be calculated knowing the entropy of a substance and the ideal gas heat capacity
 - can be calculated as a departure function $\frac{\mu - \mu^{ig}}{RT} = \ln \phi$ where ϕ is the fugacity coefficient. The fugacity coefficient can be determined from dimensionless diagrams or from equations of state
 - can be calculated as a departure function $\frac{\mu - \mu^{ig}}{RT} = \ln \phi$ where ϕ is the compressibility factor. The departure function can be determined from dimensionless diagrams

9. Partial molar property \bar{M}_i of substance i is:

- defined as $\left(\frac{\partial M}{\partial n_i} \right)_{p,V,n_{j \neq i}} = \bar{M}_i$
- defined as $\left(\frac{\partial M}{\partial n_i} \right)_{p,T,n_{j \neq i}} = \bar{M}_i$
- defined as $\left(\frac{\partial M}{\partial n_i} \right)_{V,T,n_{j \neq i}} = \bar{M}_i$
- defined as $\left(\frac{\partial M}{\partial n_i} \right)_{T,n_{j \neq i}} = \bar{M}_i$

Meerkeuzevragen 10-12: over exergie en stoomkringprocessen

Opgave 1

- a) Derive an equation for the changes of the internal energy, $d\bar{u}$, that can be evaluated with an equation of state $f(p, V, T)$ and a heat capacity. Start from

$$d\bar{u} = \left(\frac{\partial \bar{u}}{\partial T} \right)_{\bar{v}} dT + \left(\frac{\partial \bar{u}}{\partial \bar{v}} \right)_T d\bar{v}$$

- b) Draw an h - T diagram of a pure substance. Label the vapor and the liquid phase and the ideal gas line
- c) Draw an isotherm of the Van der Waals equation of state where a liquid and a vapor coexist. Show the regions of stability, metastability, and instability
- d) Make a diagram of the chemical potential with temperature of a vapor. Support your diagram with the equation of the chemical potential of an ideal gas.
- e) Is the pressure of a real gas (for given \bar{v}, T) always lower than the ideal-gas; is it always higher; or can it be both lower or higher? Support your answer with a diagram of the second virial coefficient $B(T)$ as a function of temperature. The virial equation of state is $p\bar{v}/(\bar{R}T) = 1 + B(T)/\bar{v}$
- f) Assume you have given a function for the Gibbs energy G as $G(p, T, n_i)$. Derive expressions for S, V, H, U, c_p
- g) Given 2 vapor pressure data points of propane ($p^{sat}(T=253.15 \text{ K})=2.444 \text{ bar}$ and $p^{sat}(T=263.15 \text{ K})=3.451 \text{ bar}$), estimate the vapor pressure at 25°C using the Clausius-Clapeyron equation.
- h) Estimate the specific enthalpy of vaporization of propane in the temperature range (in units kJ/kg) given in problem g). **The molecular mass of propane is $M_{\text{C}_3\text{H}_8}=44.1 \text{ g/mol}$.**

Opgave 2

Ethylene at 320 K and 20 bar enters a compressor operating at steady state and is compressed to 100 bar with an outlet temperature of 380 K. The heat addition (negative) is $\dot{Q}_{cv} / \dot{m} = -74.0 \text{ kJ/kg}$. Kinetic and potential energy changes are negligible.

Molecular mass of ethylene is $M_{\text{Ethylene}} = 28.05 \text{ g/mol}$; the ideal-gas heat capacity can be treated as constant with $c_p^{ig} = 84.0 \text{ J/(mol K)}$ in the considered temperature range. The heat transfer can be assumed to be realized at the average temperature of $T^{trans} = 350 \text{ K}$.

Using the departure function diagrams

- Evaluate the work required (in kJ per kg of ethylene flowing through the compressor) **assuming the absence of internal irreversibilities**
- Calculate the entropy production (per kg of ethylene flowing through the compressor)

Recalculate the enthalpy departure function for the inlet condition using the virial equation of state $p\bar{v}/(\bar{R}T) = 1 + B(T)/\bar{v}$:

- Calculate the molar volume at the inlet condition according to the virial equation of state
- Derive the formula for the enthalpy departure from the virial equation of state
- Estimate the enthalpy departure function at the inlet condition.

$$B(T=310\text{K}) = -129.0 \text{ cm}^3/\text{mol}$$

$$B(T=320\text{K}) = -120.0 \text{ cm}^3/\text{mol}$$

$$B(T=330\text{K}) = -111.0 \text{ cm}^3/\text{mol}$$

Opgave 3

(over exergie en stoomkringprocessen)

Meerkeuzevragen

- 1 C
- 2 B
- 3 A
- 4 $U(V, S, n_i)$ er zat nog een fout in de opgave (nieuwe versie staat op BB)
- 5 D
- 6 D
- 7 C
- 8 C
- 9 B

opgave 1

a) find \bar{u} as a fct. of p, T, \bar{v} and c_v or c_p

$$d\bar{u} = \left(\frac{\partial \bar{u}}{\partial T}\right)_{\bar{v}} dT + \left(\frac{\partial \bar{u}}{\partial \bar{v}}\right)_T d\bar{v}$$

$\leftarrow c_v$

$$\downarrow$$
$$d\bar{u} = T d\bar{s} - p d\bar{v}$$

\Downarrow

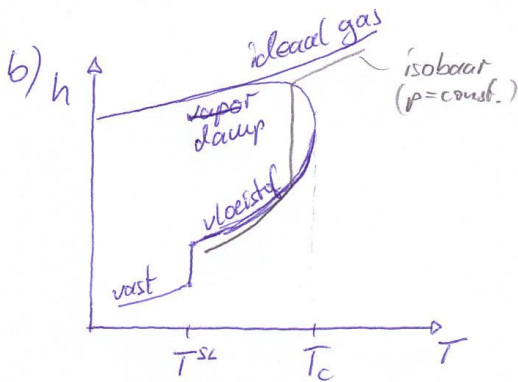
$$\left(\frac{\partial \bar{u}}{\partial \bar{v}}\right)_T = T \left(\frac{\partial \bar{s}}{\partial \bar{v}}\right)_T - p \left(\frac{\partial \bar{v}}{\partial \bar{v}}\right)_T$$

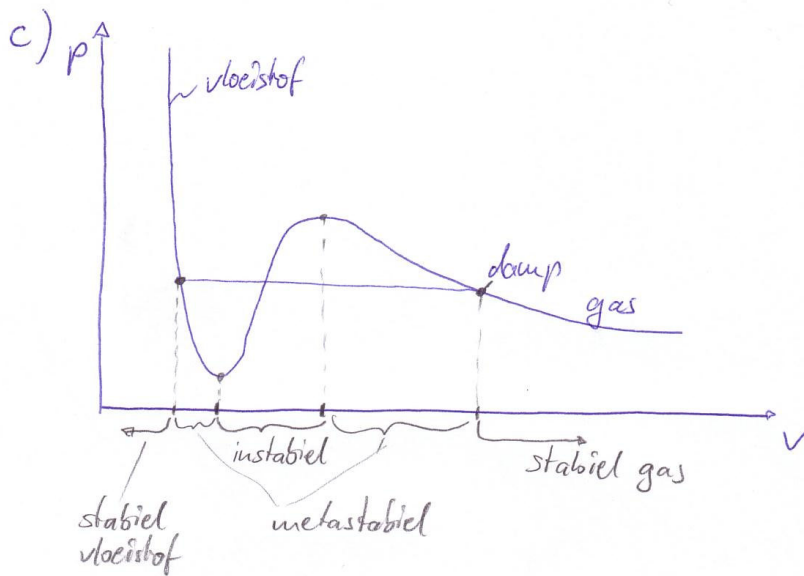
$\leftarrow 1$

$\leftarrow \left(\frac{\partial p}{\partial T}\right)_{\bar{v}}$ Maxwell relations

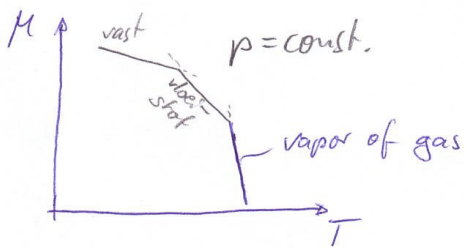
$$\begin{array}{c} -\bar{s} \cdot \bar{u} \bar{v} \\ \bar{h} \quad \parallel \quad \bar{f} \\ -p \quad \bar{g} \quad \bar{T} \end{array}$$

$$\Rightarrow d\bar{u} = c_v dT + \left[T \left(\frac{\partial p}{\partial T}\right)_{\bar{v}} - p \right] d\bar{v}$$





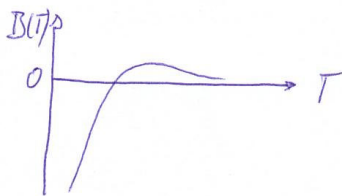
d) chemisch potentiaal als fct. van T



$\mu = \bar{g}$ en $\bar{g}(p, T)$ pure comp.
 $\Rightarrow d\bar{g} = \left(\frac{\partial \bar{g}}{\partial p}\right)_T dp + \left(\frac{\partial \bar{g}}{\partial T}\right)_p dT$
 $d\bar{g} = \bar{v} dp + (-\bar{s}) dT$
 $\Rightarrow d\mu = -\bar{s} dT$ voor $p = \text{const.}$
 \Rightarrow negatieve helling

e) viriaal toestandsverg. $Z = \frac{p\bar{v}}{RT} = 1 + B(T) \frac{1}{v}$

$\underbrace{\hspace{2cm}}$
 ideaal gas kan groter
 aandeel en kleiner
 zijn als 0



$\Rightarrow p$ van reëel gas kan groter of kleiner zijn als $p_{\text{ideaal gas}}$

f) $S = - \left(\frac{\partial G}{\partial T} \right)_p$ from $\begin{matrix} -S & U & V & + \\ H & & & F \\ -p & G & T & + \end{matrix}$

$V = + \left(\frac{\partial G}{\partial p} \right)_T$

$H = ? \quad G = H - TS \Rightarrow H = G - T \left(\frac{\partial G}{\partial T} \right)_p \quad (*)$

$U = ? \quad G = U + pV - TS \Rightarrow U = G - p \left(\frac{\partial G}{\partial p} \right)_T + T \left(\frac{\partial G}{\partial T} \right)_p$

$C_p = ? \quad C_p = \left(\frac{\partial H}{\partial T} \right)_p = \left(\frac{\partial G}{\partial T} \right)_p - \left\{ \left(\frac{\partial G}{\partial T} \right)_p + T \left(\frac{\partial^2 G}{\partial T^2} \right)_p \right\}$
↑ net (*)

$C_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p$

g) $p_1 = p^{sat}(253.15K) = 2.444 \text{ bar}$
 $p_2 = p^{sat}(263.15K) = 3.451 \text{ bar}$
 $p_3 = p^{sat}(298.15K) = ?$

Clausius - Clapeyron $\ln \frac{p_2}{p_1} = - \frac{\Delta^{vap} \bar{h}}{\bar{R}} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$

$\Rightarrow \frac{\Delta^{vap} \bar{h}}{\bar{R}} = - \frac{\ln \frac{p_2}{p_1}}{\frac{1}{T_2} - \frac{1}{T_1}} = \frac{\ln \frac{3.451}{2.444}}{\frac{1}{263.15K} - \frac{1}{253.15K}} = 2298 \text{ K}$

$\ln \frac{p_3}{p_2} = - \frac{\Delta^{vap} \bar{h}}{\bar{R}} \left(\frac{1}{T_3} - \frac{1}{T_2} \right)$

$\Rightarrow p_3 = p_2 \cdot \exp \left(- \frac{\Delta^{vap} \bar{h}}{\bar{R}} \left(\frac{1}{T_3} - \frac{1}{T_2} \right) \right)$
 $= 3.451 \text{ bar} \cdot \exp \left(-2298 \text{ K} \left(\frac{1}{298.15K} - \frac{1}{263.15K} \right) \right)$

$p_3 = 9.62 \text{ bar}$

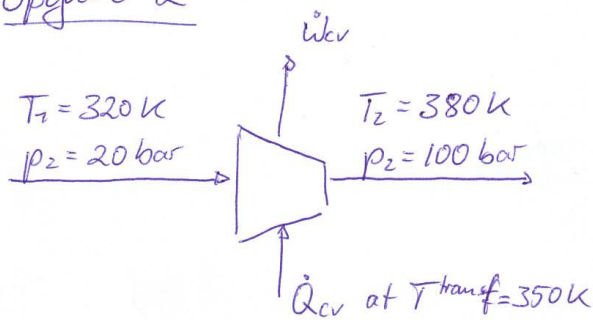
h) wij hadden in g) :

$$\frac{\Delta_{\text{vap}} \bar{h}}{\bar{R}} \approx 2298 \text{ K} \quad \text{voor} \quad 253 \text{ K} < T < 263 \text{ K}$$

$$\Delta_{\text{vap}} \bar{h} = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \cdot 2298 \text{ K} = 19.11 \frac{\text{kJ}}{\text{mol}}$$

$$\Delta_{\text{vap}} h = \Delta_{\text{vap}} \bar{h} / M_{\text{propane}} = \frac{19.110 \frac{\text{kJ}}{\text{kmol}}}{44.1 \frac{\text{kg}}{\text{kmol}}} = 435 \frac{\text{kJ}}{\text{kg}}$$

oppgave 2



- steady state
- kinetic & potential energy changes $\neq 0$
- compressor: \dot{W}_{cv} has to be negative (opposite to direction of arrow)
- $\dot{Q}_{cv}/\dot{m} = -74,0 \frac{\text{kJ}}{\text{kg}}$

ethylene: $M_{C_2H_4} = 28,05 \frac{\text{g}}{\text{mol}}$

$c_p^{ig} = 84,0 \frac{\text{J}}{\text{mol} \cdot \text{K}}$

$T_c = 283 \text{ K}$, $p_c = 51,2 \text{ bar}$ (mit tabel van Moran & Shapiro)

preparing the use of departure fct. diagrams (A-4 & A-5)

$TR_1 = \frac{T_1}{T_c} = \frac{320 \text{ K}}{283 \text{ K}} = 1,13$

$TR_2 = 1,34$

$PR_1 = \frac{p_1}{p_c} = \frac{20 \text{ bar}}{51,2 \text{ bar}} = 0,39$

$PR_2 = 1,95$

from A-4 & A-5:

$\left(\frac{\bar{h} - \bar{h}^{ig}}{RT_c}\right)_1 = -0,3$

$\left(\frac{\bar{h} - \bar{h}^{ig}}{RT_c}\right)_2 = -1,65$

$\left(\frac{\bar{s} - \bar{s}^{ig}}{R}\right)_1 = -0,25$

$\left(\frac{\bar{s} - \bar{s}^{ig}}{R}\right)_2 = -0,75$

balance eq.s.

mass balance: $\frac{d\dot{m}_{cv}}{dt} = \dot{m}_1 - \dot{m}_2 := \dot{m}$

energy bal.: $\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_1 \left(h_1 + \frac{c_1^2}{2} + g z_1 \right) - \dot{m}_2 \left(h_2 + \frac{c_2^2}{2} + g z_2 \right)$
kinetic & pot. en.

$\Rightarrow \frac{\dot{W}_{cv}}{\dot{m}} = \frac{\dot{Q}_{cv}}{\dot{m}} - (h_2 - h_1)$

entropy balance
(second law)

$$\frac{dS_{cv}}{dt} = \frac{\dot{Q}_{cv}}{T_{transf}} + \dot{m}_1 s_1 - \dot{m}_2 s_2 + \dot{G}_{cv}$$

$$\Rightarrow \frac{\dot{Q}_{cv}/\dot{m}}{T_{transf}} = (s_2 - s_1) - \dot{G}_{cv}/\dot{m}$$

a) $\frac{\dot{W}_{cv}}{\dot{m}} = ?$

$$\frac{\dot{W}_{cv}}{\dot{m}} = \frac{\dot{Q}_{cv}}{\dot{m}} - (h_2 - h_1)$$

$$= \frac{\dot{Q}_{cv}}{\dot{m}} - \frac{1}{\text{Methy.}} [h_2 - h_1]$$

$$\text{mit } [h_2 - h_1] = [(h - h^{ig})_2 - (h - h^{ig})_1 + (h_2^{ig} - h_1^{ig})]$$

$$= \frac{\dot{Q}_{cv}}{\dot{m}} - \frac{1}{\text{Methy.}} \left[\bar{R} T_c \left\{ \left(\frac{h - h^{ig}}{\bar{R} T_c} \right)_2 - \left(\frac{h - h^{ig}}{\bar{R} T_c} \right)_1 \right\} + (h_2^{ig} - h_1^{ig}) \right]$$

$$(h_2^{ig} - h_1^{ig}) = \int_{T_1}^{T_2} c_p^{ig} dT$$

$$= c_p^{ig} (T_2 - T_1)$$

$$= -74 \frac{\text{kJ}}{\text{kg}} - \frac{1}{28.05 \frac{\text{kg}}{\text{kmol}}} \left[8.314 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \cdot 283 \text{K} \left\{ -1.65 + 0.3 \right\} + 84 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} (380 - 320) \text{K} \right]$$

$$= (-74 - 66.4) \frac{\text{kJ}}{\text{kg}}$$

$$\frac{\dot{W}_{cv}}{\dot{m}} = -140.4 \frac{\text{kJ}}{\text{kg}}$$

c) $\frac{\dot{G}_{cv}}{\dot{m}} = ?$

$$\frac{\dot{G}_{cv}}{\dot{m}} = - \frac{\dot{Q}_{cv}/\dot{m}}{T_{transf}} + s_2 - s_1$$

$$= \frac{1}{\text{Methy.}} \left[(\bar{s} - \bar{s}^{ig})_2 - (\bar{s} - \bar{s}^{ig})_1 + (\bar{s}_2^{ig} - \bar{s}_1^{ig}) \right]$$

$$= \frac{1}{\text{Methy.}} \left[\bar{R} \left\{ \left(\frac{\bar{s} - \bar{s}^{ig}}{\bar{R}} \right)_2 - \left(\frac{\bar{s} - \bar{s}^{ig}}{\bar{R}} \right)_1 \right\} + (\bar{s}_2^{ig} - \bar{s}_1^{ig}) \right]$$

$$\begin{aligned}
\bar{s}_2^{ig} - \bar{s}_1^{ig} &= \int_{T_1}^{T_2} \frac{c_p^{ig}}{T} dT - \bar{R} \ln \frac{p_2}{p_1} \\
&= c_p^{ig} \ln \frac{T_2}{T_1} - \bar{R} \ln \frac{p_2}{p_1} \\
&= 84 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \ln \frac{380}{320} - 8.314 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \ln \frac{100}{20} \\
&= 1.055 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}}
\end{aligned}$$

$$\frac{\dot{G}_{av}}{\dot{m}} = + \frac{74 \frac{\text{kJ}}{\text{kg}}}{350 \text{K}} + \frac{1}{28.05 \frac{\text{kg}}{\text{kmol}}} \left[8.314 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \cdot \{-0.75 + 0.25\} + 1.055 \frac{\text{kJ}}{\text{kmol} \cdot \text{K}} \right]$$

$$\frac{\dot{G}_{av}}{\dot{m}} = 0.101 \frac{\text{kJ}}{\text{kg} \cdot \text{K}}$$

c) $\frac{p\bar{v}}{RT} = 1 + B(T) \frac{1}{\bar{v}} \Leftrightarrow \bar{v}^2 - \frac{RT}{p} \bar{v} - B(T) \frac{RT}{p} = 0$

$$\Rightarrow \bar{v} = \frac{1}{2} \left[+ \frac{RT}{p} + \sqrt{\left(\frac{RT}{p}\right)^2 + 4B(T) \left(\frac{RT}{p}\right)} \right]$$

met $\left(\frac{RT}{p}\right) = \frac{8.314 \cdot 320 \frac{\text{J}}{\text{mol}}}{20 \cdot 10^5 \frac{\text{J}}{\text{m}^3}} = 1330 \frac{\text{cm}^3}{\text{mol}}$

$$\Rightarrow \bar{v} = 1197 \frac{\text{cm}^3}{\text{mol}}$$

d) $(\bar{h} - \bar{h}^{ig})_v = \bar{R}T(Z-1) + \int_{\infty}^{\bar{v}} \left[T \left(\frac{\partial p}{\partial T}\right)_v - p \right] d\bar{v}$

met viriaal vergel. $Z = \frac{p\bar{v}}{RT} = 1 + B(T) \frac{1}{\bar{v}} \Rightarrow p = RT \frac{1}{\bar{v}} + B(T) \cdot RT \frac{1}{\bar{v}^2}$

$$\left(\frac{\partial p}{\partial T}\right)_v = \bar{R} \frac{1}{\bar{v}} + \left\{ \frac{dB}{dT} \cdot RT \frac{1}{\bar{v}^2} + B(T) \cdot \bar{R} \frac{1}{\bar{v}^2} \right\}$$

$$T \left(\frac{\partial p}{\partial T}\right)_v = \underbrace{RT \frac{1}{\bar{v}} + B(T) \cdot RT \frac{1}{\bar{v}^2}}_{= p} + \bar{R} T \frac{1}{\bar{v}^2} \frac{dB}{dT}$$

$$\Rightarrow (\bar{h} - \bar{h}^{ig})_v = \bar{R}T B(T) \frac{1}{\bar{v}} + \int_{\infty}^{\bar{v}} \left(\bar{R} T \frac{1}{\bar{v}^2} \frac{dB}{dT} \right) d\bar{v}$$

$$= \bar{R} T \frac{dB}{dT} \int_{\infty}^{\bar{v}} \frac{1}{\bar{v}^2} d\bar{v} = -\bar{R} T \frac{1}{\bar{v}} \frac{dB}{dT}$$

$$= \left[-\frac{1}{\bar{v}} \right]_{\infty}^{\bar{v}} = -\frac{1}{\bar{v}} + 0$$

$$(\bar{h} - \bar{h}^{ig})_v = \bar{R}T \frac{1}{\bar{v}} \left[B(T) - T \left(\frac{dB}{dT}\right) \right]$$

$$e) \frac{dB}{dT} = \frac{-111 + 120 \frac{\text{cm}^3}{\text{mol} \cdot \text{K}}}{330 - 320} = 0.9 \frac{\text{cm}^3}{\text{mol} \cdot \text{K}} \quad (\text{at } 320\text{K})$$

$$\begin{aligned} (\bar{h} - \bar{h}^{\text{ig}})_1 &= 8.314 \cdot 320 \frac{\text{kJ}}{\text{kmol}} \cdot \frac{1}{1197 \frac{\text{cm}^3}{\text{mol}}} \left[-120 \frac{\text{cm}^3}{\text{mol}} - 320 \text{K} \cdot 0.9 \frac{\text{cm}^3}{\text{mol} \cdot \text{K}} \right] \\ &= -907 \frac{\text{kJ}}{\text{kmol}} \end{aligned}$$

$$e) \frac{191}{98} = 1.95$$