※ 考生請注意：本試題 ☑可 ☐不可 使用計算機

1. (16%) For a gas obeys van der Waals equation $\left(P+\frac{a}{V_m{}^2}\right)(V_m-b)=RT$

(a) Show that $\left(\frac{\partial U}{\partial V_m}\right)_T=\frac{a}{V_m{}^2}$ (7 %)

(b) Suppose that a gas obeys the van der Waals equation and that two parameters, a and b, have values of 0.1408 Pa m^6 mol^{-2}, and 0.0391 dm^3 mol^{-1}, respectively. If 2.0 mol of the gas at 25 °C is reversibly and isothermally compressed from an initial volume of 2.00 dm^3 to a final volume of 0.500 dm^3, calculate q, w, ΔU and ΔH. **(9 %)**

2. (17%)

(a) Calculate the heat of combustion for 1 mol of methane burnt completely in air at 25°C. **(5%)**

(b) What is the maximum temperature that can be reached by the combustion of methane with 20% excess in air ? Both the methane and the air enter the burner at 25°C. **(12%)**

Given:

	ΔH_f^o (25°C)	$C_P{}^{o*}$	
	(kJ mol^{-1})	A (J K^{-1} mol^{-1})	10^3B (J K^{-2} mol^{-1})
$CH_4(g)$	-74.52	14.15	75.50
$H_2O(g)$	-241.82	30.54	10.29
$H_2O(l)$	-285.83	75.48	0
$CO_2(g)$	-393.51	44.22	8.79
$O_2(g)$	0	29.96	4.18
$N_2(g)$	0	28.58	3.76

*: $C_P{}^o = A + BT$ is used over the working temperature region.

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3. (16%) $dH = -udu = TdS + VdP$ For isentropic ideal gas flow in a tube with a throat, please derive to obtain the following three equations (1)-(3)

(1) $u_2^2 - u_1^2 = -2\int_{P_1}^{P_2} VdP = \dfrac{2\gamma P_1 V_1}{\gamma - 1}\cdot\left[1 - \left(\dfrac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}\right]$

(2) $u_2^2 = \gamma P_2 V_2$ (for $u_1 = 0$)

(3) $\dfrac{P_2}{P_1} = \left(\dfrac{2}{\gamma+1}\right)^{\gamma/\gamma-1}$ (the pressure ratio at the throat)

[Note] For isentropic ideal gas, $PV^\gamma = \text{constant}$, also, $u_2^2 = c^2 \equiv -V^2 \cdot \left(\dfrac{\partial P}{\partial V}\right)_S$ where c is the speed of sound.

4. (18%) Answer False (F) or true (T). For those false, please give your explanation. (3% each)

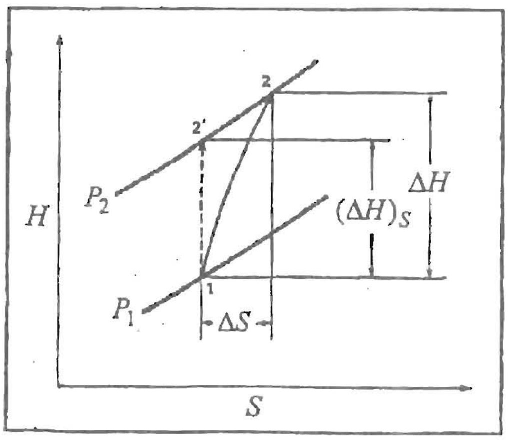
(a) entropy change of the system is always non-negative.

(b) entropy change of mixing is always non-negative.

(c) Carnot engine is the only reversible heat engine.

(d) Water flows in a pipe at 3 m/s. A valve at the end of the pipe is suddenly closed. Then, the pressure in the pipe is dropped.

(e) $\lim_{P \to 0} V^R = 0$

(f) 

This may interpret the H vs. S diagram of a turbine from state 1 to state 2.

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5. (33%) Consider a binary system consisting of both vapor and liquid phases in equilibrium. Please answer the following questions:

(a) First consider the liquid phase. Let x_1 and x_2 be the respective mole fractions of component 1 and 2. At constant temperature and pressure, the molar excess Gibbs free energy G^E is given by

$$G^E = RTx_1x_2^{\ 2}.$$

Find the partial excess Gibbs free energy $\bar{G}_i^E$ and the activity coefficient γ_i for each component.

Also determine the liquid fugacity $\hat{f}_i^L$ in terms of x_i and the fugacity at *pure* state, f_i^L. $R = 8.314$ Joule mole^{-1} K^{-1} is the gas constant. **(9%)**

(b) As for the vapor phase, its PVT behavior can be described by

$$\frac{PV}{RT} = 1 + \frac{BP}{RT}.$$

Here the second virial coefficient is given by $B = y_1B_1 + y_2B_2$ with y_i and B_i standing respectively for the mole fraction and the virial coefficient for component i (=1,2). Determine the partial residual Gibbs free energy $\bar{G}_i^R$ and the vapor fugacity coefficient $\hat{\phi}_i$ for each component. **(8%)**

(c) Write the expression for the fugacity at *pure* state f_i^L in terms of the saturated vapor pressure P_i^{sat} and the corresponding fugacity coefficient ϕ_i^{sat}. Assume that f_i^L is insensitive to the vapor pressure P. Also use the results in (b) to determine f_i^L in terms of P_i^{sat} and B_i. **(8%)**

(d) At temperature T=300K the liquid composition is known, say, $x_1 = 0.5$. Find the vapor pressure and composition. You will need to use the results in (a)-(c) and the data below to solve this problem. $B_1 = 2.4942$ m^3/mole, $B_2 = 4.9884$ m^3/mole, P_1^{sat} =0.5kPa, P_2^{sat} =1kPa. **(8%)**