1. What is the change in entropy of a system when  $5\ kJ$  of energy is

transferred reversibly from the system to the surroundings as heat in

an exothermic process at a temperature of 21°C?

- $\odot$  -17 J K<sup>-1</sup>
- $\bigcirc$  -5000 J K<sup>-1</sup>
- $\bigcirc$  +5000 J K<sup>-1</sup>
- $\bigcirc$  +17 J K<sup>-1</sup>

## ✓ Correct

The 2nd Law of Thermodynamics may be expressed quantitatively as

 $\Delta S = q_{rev}/T.$  Since  $5~\mathrm{kJ}$  leave the system

 $-5\ \mathrm{kJ}$  are transferred to the system at constant temperature

and  $q_{rev}=-5000~\mathrm{J}$  . Thus  $\Delta S=-5000~\mathrm{J}/294~\mathrm{K}=-17~\mathrm{J}~\mathrm{K}^{-1}$  .

2. What is the change in the standard molar entropy of sulphur trioxide

gas,  $SO_3$ , when it is cooled from a temperature of  $90^{\circ}\mathrm{C}$  to  $20^{\circ}\mathrm{C}$  at a constant pressure of 1 bar? The standard molar constant-pressure heat capacity of sulphur trioxide,

$$C_{p,m}^{\ominus}$$
, is 50.1 J K<sup>-1</sup> mol<sup>-1</sup>.

- $\cap$  +10.7 J K<sup>-1</sup> mol<sup>-1</sup>
- $\bigcirc$  -10.7 J K<sup>-1</sup> mol<sup>-1</sup>
- $\bigcirc$  -75.4 J K<sup>-1</sup> mol<sup>-1</sup>
- $\bigcirc$  +75.4 J K<sup>-1</sup> mol<sup>-1</sup>

#### ✓ Correct

Since  $\Delta S = C \ln(T_f/T_i)$  and the process occurs at  $1 \, \mathrm{bar}$ ,

$$\Delta S_m = C_{p,m}^{\ominus} \ln(T_f/T_i) = 50.1 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln(293K/363K) = -10.73 \text{ J K}^{-1} \text{ mol}^{-1}.$$

3.	Which of the following statements concerning the reaction Gibbs energy		
	is INCORRECT?		
	0	Equilibrium is attained when the reaction Gibbs energy is equal to	
		zero.	
	•	The reaction Gibbs energy can never be positive.	
	$\bigcirc$	The reaction Gibbs energy is the difference between the chemical	
		potentials of the products and the reactants at the composition of	
		the reaction mixture.	
	$\bigcirc$	The reaction Gibbs energy may be thought of as the slope of a graph	
		of Gibbs energy against composition of the system.	

# ✓ Correct

The reaction Gibbs energy can be positive, negative or zero. If the reaction Gibbs energy is negative then the forwards reaction is spontaneous and if the reaction Gibbs energy is positive then the backwards reaction is spontaneous. When the reaction Gibbs energy is zero the reaction is at equilibrium.

 The carbonylation of methanol yields ethanoic acid according to the equation given below:

$$CH_3OH(g) + CO(g) \leftrightarrow CH_3COOH(g)$$

Using the following table of thermodynamic data at  $298~\mathrm{K}$ :

Substance	$\Delta_f H^{\Theta} / \text{ kJ mol}^{-1}$	$S^{\Theta}$ / J K <sup>-1</sup> mol <sup>-1</sup>
$CH_3OH(g)$	-201	240
CO(g)	-110	198
$CH_3COOH(g)$	-432	283

What are the standard molar reaction enthalpy and the standard molar

reaction entropy associated with this reaction at  $298~\mathrm{K}$ ?

- $\bigcirc \ +121 \ kJ \ mol^{-1} \ and \ -155 \ J \ K^{-1} \ mol^{-1}$
- $\bullet$  -121 kJ mol<sup>-1</sup> and 155 J K<sup>-1</sup> mol<sup>-1</sup>
- $\bigcirc$  -121 kJ mol<sup>-1</sup> and + 155 J K<sup>-1</sup> mol<sup>-1</sup>
- $\bigcirc$  +121 kJ mol<sup>-1</sup> and + 155 J K<sup>-1</sup> mol<sup>-1</sup>

#### ✓ Correct

$$\Delta H^{\ominus} = 1 \times (-432) - 1 \times (-201) - 1 \times (-110) \text{ kJ mol}^{-1} = -121 \text{ kJ mol}^{-1}$$

$$\Delta S^{\ominus} = 1 \times (+283) - 1 \times (+240) - 1 \times (+198) + JKmol^{-1} = -155~\mathrm{J~K^{-1}~mol^{-1}}$$

- 5. For the reaction in Q4 what is the standard molar reaction Gibbs energy?
  - $-74.8 \text{ kJ mol}^{-1}$
  - $\bigcirc$  -92.6 kJ mol<sup>-1</sup>
  - $\bigcirc$  -111.5 kJ mol<sup>-1</sup>
  - $\bigcirc$  -134.0 kJ mol<sup>-1</sup>

#### ✓ Correct

 $\Delta G = \Delta H - T \Delta S = -121,000 \text{ J mol}^{-1} - (298K \times -155 \text{ J K}^{-1}) = (-121,00 + 46190) \text{ J mol}^{-1} = -74810 \text{ J mol}^{-1} = -74.8 \text{ kJ mol}^{-1}.$ 

- 6. For the reaction in Q4 what is the thermodynamic equilibrium constant?
  - $\bigcirc$  1.299  $\times$  10<sup>15</sup>
  - (a)  $1.299 \times 10^{13}$
  - $\bigcirc$  1.299 × 10<sup>19</sup>
  - $\bigcirc$  1.299 × 10<sup>11</sup>

### ✓ Correct

 $\Delta_r G^\ominus = -RT \ln {\rm K}$  and thus  ${\rm K} = e^{\Delta r G^\ominus/RT} = e^{-(-74.8~{\rm kJ~mol}^{-1})/(8.314~{\rm J~K}^{-1}~{\rm mol}^{-1}\times 298~{\rm K})} = e^{30.2} = 1.299\times 10^{13}$ 

- 7. Close to absolute zero the heat capacity of non-metallic substances at constant volume, in accordance with the Debye Law, approximates to which of the following temperature dependences?
  - $\bigcirc C_{V,m} \alpha 1/T$   $\bigcirc C_{V,m} \alpha T^2$

  - $C_{V,m} \alpha T$   $C_{V,m} \alpha T^3$

# Correct

This law is stated on slide seven of the video on the Third Law of

Thermodynamics and Absolute Entropy.

8. What is the molar reaction enthalpy of the reaction between ethane

gas and fluorine gas

$$C_2H_4(g) + 6F_2(g) \rightarrow 2CF_4(g) + 4HF(g)$$

given the following thermodynamic data?

$H_2(g) + F_2(g) \rightarrow 2HF(g)$	$\Delta_r H_m = -537 \text{ kJ mol}^{-1}$
$C(s) + 2F_2(g) \rightarrow CF_4(g)$	$\Delta_r H_m = -680 \text{ kJ mol}^{-1}$
$2C(s) + 2H_2(g) \rightarrow C_2H_4(g)$	$\Delta_r H_m = +52 \text{ kJ mol}^{-1}$

- $-2486 \text{ kJ mol}^{-1}$
- $\bigcirc$  -945 kJ mol<sup>-1</sup>
- $\bigcirc$   $-1942~kJ~mol^{-1}$
- $\bigcirc$  -1387 kJ mol<sup>-1</sup>

#### ✓ Correct

The desired equation is equivalent to 2 reaction one, 2 reaction two

and reaction three backwards. Thus  $\Delta_r H_m = (2 \times -537) + (2 \times -680) + (-1 \times 52) \text{ kJ mol}^{-1} = -2486 \text{ kJ mol}^{-1}$ 

9. Given the following data at  $298~{
m K}$ , what is the standard enthalpy of reaction for the addition of hydrogen chloride, HCl, to ethene,

$$C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$$

Substance	$\Delta_f H^{\Theta} / \text{kJ mol}^{-1}$
$C_2H_4(g)$	+52.2
HCl(g)	-92.3
$C_2H_5Cl(g)$	-109.8

 $\bigcirc$  149.9 kJ mol<sup>-1</sup>

 $C_2H_4$  at 298 K?

- $\bigcirc$  254.3 kJ mol<sup>-1</sup>
- $\bigcirc$  -69.7 kJ mol<sup>-1</sup>
- $\bigcirc$  -34.7 kJ mol<sup>-1</sup>

### ✓ Correct

$$\Delta H^{\ominus} = 1 \times (-109.8) - 1 \times (+52.2) - 1 \times (-92.3) \text{ kJ mol}^{-1} = -69.7 \text{ kJ mol}^{-1}$$

10. A reaction has an enthalpy change of  $+14~{
m kJ~mol^{-1}}$  and an

entropy change of  $+37~\mathrm{J~K^{-1}~mol^{-1}}$ . At what

temperature does this endothermic reaction become spontaneous?

- 54°C
- 76°C
- 98°C
- 105°C

### ✓ Correct

 $\Delta G = \Delta H - T \Delta S$ . When the reaction switches

spontaneity  $\Delta G=0$  and thus  $0=\Delta H-T\Delta S$  and  $T\Delta S=\Delta H$  and  $T=\Delta H/\Delta S=+14,000~\mathrm{J~mol}^{-1}/+37~\mathrm{J~K}^{-1}~\mathrm{mol}^{-1}=378~\mathrm{K}=105^{\circ}C.$